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Especialização em Hidrogeologia

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Projeto de investigação orientado por:
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## Abstract

Soil-Aquifer Treatment (SAT) is a well-established Managed Aquifer Recharge (MAR) complementary method which main purpose is to increase water availability in aquifers by enhancing the quality of the injected water. SAT-MAR methods are an important way of addressing water scarcity challenges by reusing water of impaired quality, such as wastewater, converting it into a reliable resource. They can be quite useful in water resource management, particularly in semi-arid regions, helping to face decrease of rainfall and long drought periods resulting from climate change. In this context, SAT can also present itself as a relatively simple and inexpensive complementary method of treatment, lessening possible environmental problems.

The research presented in this dissertation was developed in the framework of EU 7th Framework Project MARSOL project which aims to demonstrate the reliability of MAR processes to face water scarcity problems in Southern Europe and Mediterranean regions. Several soil characterization, soil-column and batch experiments were conducted at National Laboratory for Civil Engineering (LNEC) using a soil collected in São Bartolomeu de Messines, one of the projects demonstration sites where SAT-MAR basins are to be constructed using treated wastewater as primary infiltration water source.

These experiments aimed to characterize the soil behaviour at lab scale by simulating infiltration basin conditions, determining hydraulic characteristics and contaminant retention capacities. Natural soil results obtained were later compared to those obtained for a soil mixture produced in LNEC. This soil mixture will act as a reactive layer to be installed in the bottom of the infiltration basins, increasing capacity to retain certain contaminants detected in inflow water, but also keeping acceptable hydraulic conductivity without hindering the water-soil interaction. The referred mixture results from a combination of cheap and easily available materials with the natural soil.

Unregulated emerging contaminant problematic was also discussed, focussing in pharmaceutical compounds, considering the type of source water used in these experiments – São Bartolomeu de Messines (SBM) wastewater treatment plant effluent. High concentration of ammonia and sulphates were measured and traces of 17 pharmaceuticals were detected.

SBM natural soil that was used in experiments is a loamy sand composed of 81.91% sand, 15.95% of silt and 2.14% clay, having quartz, calcite, montmorillonite and anorthite as major mineral constituents and traces of dolomite, illite, kaolinite and hematite. It has 24.02% of carbonates percentage, low organic matter content (2.66%), average bulk density of 1.44 g/cm$^3$ and average porosity of 43.6%.

Five soil-column experiments were conducted in this soil for different time lengths, testing different methods of column assembling, thickness, soil packing, saturation conditions and injection method (Column 1 to 5 – C1 to C5). For the three different soil mixtures produced, four soil column experiments were conducted (Column 6 to 9 – C6 to C9). Outflow samples were collected for the experiments that used wastewater as injection source (C3 to C5 and C8 and C9) – metals, nitrogen cycle components, major ions and pharmaceuticals were analysed. Pharmaceuticals were not measured for C3 inflow.

Considering hydraulic behaviour for natural soil, and taking as reference the first day of experiment, C5 showed highest flow rate (1.504 cm$^3$/min) and permeability (2.536 m/d) while

C4 showed the worst results (0.363 $cm^3$/min and 0.589 m/d). For soil mixture behaviour, C6 had higher flow rate and permeability (7.722 $cm^3$/min 12.579 m/d) but this one along C7 suffered high soil washing out along the experiment.

Concerning inflow water quality, from 32 parameters analysed (excluding pharmaceuticals), C3 had 17 values above the limit of recovery (LOR), C4 and C5 had 17 and C8 and C9 had 26. For pharmaceuticals, from the 24 parameters analysed, 14 were above LOR in C4 and C5 inflow, while in C8 and C9, nine parameters were above LOR.

Comparing the outflow in terms of quality, and more precisely average concentration of metals, from 11 parameters considered, C3 has 7 parameters where outflow concentration is higher than inflow, while C4 has 6 and C5 has 9. C8 has only 3 parameters in which outflow average concentration surpasses the inflow, although inflow sample presents a slight enrichment in certain metals when compared to other columns. Phosphorus shows the highest reduction in all columns. For nitrogen cycle components, ammonia showed high concentration at inflow and a reduction at outflow for all columns, while nitrites present low concentration at inflow and high concentration at outflow. C3, C5 and C8 show higher average concentration of nitrates when compared to inflow. Concentration at outflow in C8 reaches 140.46 mg/L, a very high value when compared to C3 (0.86 mg/L) and C5 (6.51 mg/L). Concerning major ions, for the 7 parameters considered, 4 were above inflow concentration C4, C5 and C8. C8 experiment shows a worse overall behaviour for these parameters than that with higher average concentrations.

Soil samples were collected and analysed after C3 and C5 experiments stopped. C3 shows almost equal concentration of boron, copper and zinc in top and bottom sections, but boron concentrations were lower. Ammonia showed higher concentrations when compared with nitrates and nitrites, being heavily retained in the soil top section, while nitrates where not detected in both sections and nitrites showed very small concentration. Phosphorous and phosphates show higher concentrations in the soil top section. From the set of selected pharmaceuticals, none showed concentrations above LOR in C3. For C5, boron and copper showed slightly lower concentrations to those detected in C3, and ammonia shows a high concentration on the top section. Nitrates and nitrites were also detected in higher concentration on column top section. Phosphorous and phosphates show lower concentrations in both sections when compared to C3 and sulphates where not detected in both sections. Caffeine was the only detected pharmaceutical compound in C5.

Batch experiments were also conducted in both natural soil and soil mixture. For the set of 32 parameters analysed in the inflow and outflow water of natural soil batch, eight showed a decrease in concentration in the outflow when compared to inflow. Highest percentage of removal is observed in aluminium, followed by iron, and the lowest in sodium. Nitrites, sulphate, barium, calcium, chromium, magnesium, manganese, nickel, vanadium and chloride showed an increased concentration in outflow. 14 of 24 pharmaceuticals analysed had values above LOR, only seven of those were persistent and were detected in the outflow (propanolol, bezafibrate, diclofenac, gemfibrozil, naproxen, indometacin and carbamazepine). For the persistent compounds, lowest removal rate was detected for naproxen while seven of the compounds showed 100% removal (atenolol, betaxolol, bisoprolol, metoprolol, sotalol e pentoxifillin). For the same set of parameters, 25 were detected in soil mixture inflow water while only 20 were detected in the outflow water. Ammonia presented the highest adsorbed amount and copper, zinc, nitrites, calcium, magnesium, manganese, potassium and chloride

showed an increase of concentration in outflow. Removal was higher in antimony and lowest in lithium. For the pharmaceuticals, 14 were above LOR in inflow water and only 1 in the outflow water. 100% removal rate was observed in atenolol, betaxolol, bisoprolol, metoprolol, propranolol, sotalol, bezafibrate, diclofenac, gemfibrozil, ibuprofen, indomethacin, naproxen and pentoxifyllin. Carbamazepine showed recalcitrant behaviour, but a relatively high removal rate (86.3%).

Transport of ammonia, nitrates and nitrites was modelled in Hydrus-1D to understand the conditions inside the column in continuous saturated conditions using C3 and C4 data. Simulations showed ammonia being retained on the top of the column whereas nitrites showed a small increase in concentration as ammonia concentration decrease. Then nitrites concentration decrease at the column bottom while nitrates concentration increased. Saturation indexes (Log SI) were determined at inflow and outflow for calcite, dolomite and hematite in C3, C4 and C8 by hydrogeochemical speciation in PHREEQC. C3 inflow water is unsaturated in calcite and dolomite and it's in equilibrium with hematite. C4 inflow solution is close to stability concerning dolomite and calcite while high Log SI for hematite was determined, showing saturation in this iron oxide. C8 inflow solution is slightly unsaturated in calcite and dolomite, and hematite Log SI is showing oversaturation at inflow. For all columns, outflow solutions are saturated in hematite, and oscillate from unsaturation to saturation in calcite and dolomite along the experiment. Inverse modelling in PHREEQC was also used in C3 to understand phase transfers that occur between inflow solution and the soil media along the experiments under invariable saturation conditions.

The natural soil shows some suitability to be used as a base infiltration layer for the SAT-MAR infiltration basins in what concerns infiltration capacity, but is expected to show some problems in the long term, with a continuous decrease of permeability. The soil mixture resulted in a more pervious material with a good long term hydraulic behaviour, with better response to cycles of saturation and non-saturation allowing the oxygenation of the soil. The sequential use of oxic/anoxic conditions is the best approach to ensure maximum attenuation efficiency, since some elements degrade better in oxic conditions, and others are degraded under anaerobic conditions. Complementarily, the increase of organic matter favoured the retention/degradation of most pharmaceuticals studied, as well as metals. It was also observed that high pH favoured the retention of metals into the soil.

**Keywords:** Soil-aquifer treatment; MAR; Pharmaceuticals; Metals.

## Resumo

As metodologias de tratamento solo-aquífero (SAT) são geralmente aplicadas no âmbito da recarga controlada de aquíferos (MAR) tendo como principal objetivo aumentar a disponibilidade de água no aquífero, melhorando a qualidade da água injetada. Apresentam-se como forma de enfrentar os desafios inerentes à escassez através da reutilização de água de fraca qualidade, como águas residuais com tratamento secundário. Podem ser úteis na gestão integrada de recursos hídricos, particularmente em regiões semiáridas e em zonas sujeitas à diminuição da precipitação com longos períodos de seca resultantes das alterações climáticas e apresentar-se como um método complementar de tratamento de água pouco dispendioso, permitindo diminuir possíveis problemas ambientais decorrentes da descarga no meio ambiente.

Os trabalhos apresentados foram desenvolvidos no âmbito do projeto MARSOL que tem como objetivo demonstrar a fiabilidade dos processos MAR como forma de enfrentar os problemas de escassez de água no sul da Europa e Mediterrâneo. Ensaios de caracterização do solo, em coluna e do tipo *batch* foram realizados no Laboratório Nacional de Engenharia Civil (LNEC), num solo recolhido na área de estudo de São Bartolomeu de Messines (SBM) onde serão construídas bacias SAT-MAR.

Estes pretenderam caracterizar o comportamento do solo à escala laboratorial, simulando as condições existentes nas bacias, determinando características hidráulicas e capacidade de retenção de contaminantes. Os resultados obtidos para o solo natural foram comparados com um segundo conjunto de ensaios realizados para um solo de mistura produzido no LNEC. Este solo de mistura actuará como camada reativa, instalada na base das bacias, permitindo o aumento da capacidade de retenção de contaminantes, assegurando uma permeabilidade aceitável.

A problemática dos contaminantes emergentes foi analisada, dando-se especial atenção a compostos farmacêuticos. A análise da presença destes compostos em águas tratadas e para consumo assume cada vez maior relevância particularmente em países desenvolvidos, tendo-se mesmo observado comportamento recalcitrante após tratamento. A qualidade do efluente da ETAR de SBM foi analisada sendo registada elevada concentração de amónia e sulfatos, sendo também detetados 17 compostos farmacêuticos.

O solo natural de SBM é uma areia argilosa composta por 81,91% de areia, 15,95% de silte e 2,14% de argila, apresentando-se quartzo, calcite, montmorilonite e anortite como principais constituintes minerais e evidenciando traços de dolomite, ilite, caulinite e hematite. Possui 24,02% de carbonatos, baixo teor de matéria orgânica (2,66%), densidade média de 1,44 g/cm$^3$ e porosidade média de 43,6%.

Cinco ensaios em coluna foram realizados para este solo tendo-se testado diferentes métodos de montagem, espessura de solo, procedimentos de compactação, variações das condições de saturação e método de injeção (Coluna 1 a Coluna 5 – C1 a C5). Para o conjunto de três solos de mistura com diferentes composições realizaram-se quatro ensaios em coluna (Coluna 6 a Coluna 9 – C6 a C9). Amostras foram recolhidas à saída das colunas onde foi injetado efluente tratado (C3 a C5 e C8 e C9) tendo-se analisado metais, componentes de ciclo de azoto, iões maiores e compostos farmacêuticos.

Considerando o comportamento hidráulico do solo natural, e tendo como referência o primeiro dia de ensaio, C5 mostrou maior caudal à saída (1,5 $cm^3$/min) e permeabilidade (2,5 m/d), enquanto C4 mostrou o pior desempenho (0,4 $cm^3$/min e 0,6 m/d). Para o solo de mistura, C6 apresentou maior caudal e permeabilidade (7,7 $cm^3$/min e 12,6 m/d). C6 e C7 apresentaram forte mobilização de partículas, com perda de espessura e criação de cavidades.

No que concerne à qualidade da água injetada nas colunas, dos 32 parâmetros analisados (excluindo os compostos farmacêuticos), C3 apresentou 17 valores acima do limite de deteção (LD), C4 e C5 apresentaram 17 e C8 e C9 apresentaram 26. Nos 24 compostos farmacêuticos analisados, 14 estavam acima do LD em C4 e C5, e 9 em C8 e C9.

Em termos de qualidade, mais precisamente na concentração média de metais, de 11 parâmetros considerados a C3 obteve 7 onde a concentração de saída foi maior que a de entrada, enquanto a C4 teve 6 e a C5 teve 9. A C8 teve apenas 3 parâmetros onde a concentração média de saída ultrapassa a de entrada, apesar de ser observável um ligeiro enriquecimento em certos metais à entrada em comparação com as restantes colunas. O fósforo mostra a maior redução em todas as colunas. Para os componentes do ciclo de azoto, a amónia apresentou elevada concentração à entrada e uma significativa redução à saída em todas as colunas, enquanto os nitritos apresentaram elevada concentração na saída comparativamente aos valores de entrada. C3, C5 e C8 mostram uma concentração média mais elevada de nitratos à saída em relação à concentração de entrada. Este parâmetro regista 140,46 mg/L à saída da C8, um valor muito elevado quando comparado com C3 (0,86 mg/L) e C5 (6,51 mg/L). Nos iões maiores, para o conjunto de 7 parâmetros, 4 estavam acima da concentração registada à entrada em C4, C5 e C8. C8 mostra um comportamento pior para esses iões com concentrações médias mais elevadas à saída.

Amostras de solo foram analisadas após a conclusão dos ensaios C3 e C5. C3 mostra semelhante concentração de boro, cobre e zinco nas secções superior e inferior. A amónia mostrou elevadas concentrações, sendo fortemente retida na seção superior do solo, enquanto nitratos não foram detetados em ambas as seções e os nitritos mostraram muito baixa concentração. Fósforo e fosfatos mostraram concentrações mais elevadas na secção superior do solo. Dos compostos farmacêuticos analisados, nenhum apresentou concentrações acima dos LD na C3. Na C5, boro e cobre apresentaram concentrações ligeiramente mais baixos para os detetados na C3. A amónia, nitratos e nitritos mostram uma maior concentração na secção superior da coluna. O fósforo e fosfatos mostram concentrações inferiores em ambas as secções quando comparados com a Coluna 3 e não foram detetados sulfatos em ambas as secções. A cafeína foi o único composto farmacêutico detetado na C5.

Nos ensaios *batch* realizados no solo natural, para o conjunto de 32 parâmetros analisados, oito mostraram uma diminuição na concentração entre a entrada e a saída. A maior percentagem de remoção foi observada para o alumínio, seguido do ferro total. A mais baixa foi registada para o sódio. Nitritos, sulfatos, bário, cálcio, crómio, magnésio, manganês, níquel, vanádio e cloreto mostraram aumento da concentração na saída. 14 de 24 compostos farmacêuticos analisados apresentaram valores acima dos LD à entrada mas apenas sete apresentaram comportamento persistente e foram detetados na saída. Os restantes compostos apresentaram 100% de remoção. Para o solo de mistura, 25 dos 32 parâmetros – em que se incluem metais, iões maiores e compostos do ciclo do azoto – apresentaram valores acima dos LD na água de entrada. Apenas 20 foram detetados na água de saída. A

amónia apresentou a maior quantidade adsorvida e o cobre, zinco, nitritos, cálcio, magnésio, manganês, potássio e cloreto mostraram um aumento de concentração à saída. A remoção foi maior em antimónio e menor para o lítio. Dos 24 fármacos considerados, 14 estavam acima do LD à entrada e apenas 1 na água de saída. As taxas de remoção de 100% foram observadas para 13 desses compostos e 1 mostrou comportamento recalcitrante.

O transporte da amónia, nitratos e nitritos foi modelado através do *software* Hydrus-1D tendo como objetivo compreender as condições dentro da coluna em regime de saturação contínua usando dados de C3 e C4. As simulações demonstraram a retenção da amónia na parte superior da coluna. Os nitritos mostraram um pequeno aumento da concentração com a diminuição da concentração de amónia. Em seguida, a concentração em nitritos decresce na parte inferior da coluna enquanto a concentração de nitratos aumentou ao longo da coluna. Os índices de saturação da calcite, dolomite e hematite foram determinados por especiação hidrogeoquímica em PHREEQC tanto para as soluções de entrada como de saída da C3, C4 e C8. A solução de entrada da C3 apresenta subsaturação em calcite e dolomite e está em equilíbrio com a hematite. A solução de entrada da C4 está perto do equilíbrio relativamente à calcite e dolomite e evidenciando saturação em hematite. A solução de entrada C8 é subsaturada em calcite e dolomite, e sobressaturada em hematite. Para todas as colunas, as soluções à saída estão saturadas em hematite, e oscilam ao longo dos ensaios entre a subsaturação e a saturação em calcite e dolomite. A modelação inversa com base nos dados da C3 permitiu compreender as transferências de fase que ocorrem entre uma solução de entrada e o solo em condições de saturação contínua.

Em conclusão, o solo natural mostra alguma aptidão para ser utilizado nas bacias SAT-MAR, podendo ocorrer a longo prazo colmatação e diminuição capacidade de infiltração. O solo de mistura apresentou maior permeabilidade e comportamento hidráulico mais regular a longo prazo, com melhor resposta aos ciclos de saturação/oxigenação, permitindo a oxigenação da coluna de solo. A variação das condições de oxidação resulta numa maior eficiência na atenuação de um maior espectro de elementos, já que alguns são degradados em ambiente oxidante. Concluiu-se também que o aumento da matéria orgânica favorece a retenção/degradação da maioria dos compostos farmacêuticos estudados, assim como de metais. Verificou-se ainda que o pH elevado favoreceu a retenção de metais no solo.

**Palavras-chave:** Tratamento solo-aquífero; Compostos farmacêuticos; Metais.

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## List of symbols

AL – Activity lines

BOD – Biological oxygen demand

CEC – Cation exchange capacity

COD – Chemical oxygen demand

DOC – Dissolved organic carbon

EC – Emerging Contaminants

ELV – Emission Limit Value

LOR – Limit of recovery

MAR – Managed Aquifer Recharge

MRV – Maximum Recommended Value

NA – Not analysed

OM – Organic matter

PV – Pore-volume

RBF – Riverbed filtration

RT – Residence time

SAT – Soil-aquifer Treatment

SBM – São Bartolomeu de Messines

SI – Saturation Index

SME – Small to medium enterprises

TC – Total Coliforms

TOC – Total organic carbon

TSS – Total soluble solids

UV – Ultra-violet

WP – Work Package

WW – Wastewater

WWTP – Wastewater Treatment Plant

# 1. Introduction

Water scarcity is currently a concerning issue, particularly in semi-arid regions, and presents itself as a global challenge to human populations. As climate change starts to be a more pressing problem that tends to result from the decrease of rainfall and long drought periods hindering water availability in both surface reservoirs and aquifers, groundwater management processes represent reliable solutions for assuring water supply in affected regions. In these climate change scenarios it is important for groundwater management entities to find innovative methodologies to maintain the sustainability of this resource. This where the application of Managed Aquifer Recharge (MAR) together with Soil-aquifer Treatment (SAT) methodologies, where the usage of recycled water (or reclaimed water) is promoted, can ultimately result in positive impacts by solving scarcity and environmental problems.

One of the main water sources for MAR is treated wastewater. Instead of direct discharge to a surface waterbody, this water may be injected into the aquifer. As it is a continuous supply of water, its reuse can represent a solution to the stress induced by increased demand, allowing for an integrated management with other types of supply, lessening impacts on the overall resource.

This dissertation focus on the use of Soil-Aquifer Treatment methodologies, at laboratory scaled experiments, with the purpose of understanding the increase in water quality induced by using specific soil types as depurative layer, giving important instructions for real scale SAT-MAR structures management.

## 1.1. Framework of this dissertation

This dissertation was developed in the context of an European Union 7$^{th}$ Framework Program project named MARSOL - Demonstrating Managed Aquifer Recharge as a Solution to Water Scarcity and Drought (www.marsol.eu) that is being developed in the Water Resources and Hydraulic Structures unit of the National Laboratory for Civil Engineering's Hydraulics and Environment department, in partnership with other European institutions and small to medium enterprises (SMEs).

As described in the Document of Work of MARSOL project, the main purpose is to demonstrate that MAR is a sound, safe and sustainable strategy that can be applied with great confidence and therefore offering a key approach for tackling water scarcity in Southern Europe and the Mediterranean regions that are facing the challenge of managing its water resources under conditions of increasing scarcity and concerns about water quality. Already, the availability of fresh water in sufficient quality and quantity is one of the major factors limiting socioeconomic development. Innovative water management strategies such as the storage of reclaimed water or excess water from different sources in MAR schemes can greatly increase water availability and therefore improve water security. For this, eight field sites were selected that will demonstrate the applicability of MAR using various water sources, ranging from treated wastewater to desalinated seawater, and a variety of technical solutions. Targets are the alleviation of the effect of climate change on water resources, the mitigation of droughts, to countermeasure temporal and spatial misfit of water availability, to sustain agricultural water supply and rural socio-economic development, to combat agricultural related pollutants, to sustain future urban and industrial water supply and to limit seawater intrusion in coastal

aquifers. Results of the demonstration sites will be used to develop guidelines for MAR site selection, technical realization, monitoring strategies, and modelling approaches, to offer stakeholders a comprehensive, state of the art and proven toolbox for MAR implementation. Further, the economic and legal aspects of MAR will be analysed to enable and accelerate market penetration. The MARSOL consortium combines the expertise of consultancies, water suppliers, research institutions, and public authorities, ensuring high practical relevance and market intimacy.

In summary, MARSOL aims to (1) demonstrate at 8 field sites that MAR is a safe and sustainable strategy to increase the availability of freshwater under conditions of water scarcity, (2) improve the state of the art of MAR applications to enable low cost high efficiency MAR solutions that will create market opportunities for European Industry and SMEs (MAR to market), (3) promote the advantages of MAR by tailored training and dissemination programs to enable and accelerate market penetration and (4) deliver a key technology to face the challenge of increasing water scarcity in southern Europe, the Mediterranean and other regions of the world.

The project is divided into 17 Work Packages (WP) guided by three Activity Lines (AL):

- Activity Line 1 or "Horizontal Activities" consists of Project Management (WP 1) and Dissemination, Exploitation & Training Activities (WP 2)
- Activity Line 2 covers the technical work performed at all the DEMO sites and includes "Demonstration Sites" Work Packages (WP 3 to WP 10).
- Activity Line 3 "Integration and Impact" groups activities that support the demonstrations activities and/or collect, evaluate, and assess data produced at the DEMO sites such as innovative monitoring techniques (WP 11), modelling (WP 12), benchmarking (WP 13), water quality issues (WP 14), economic feasibility considerations (WP 15), risk and contingency plans (WP 16), and legal issues and knowledge transfer for policy and governance (WP 17).

This project started in December 2013 and finishes in December 2016, being coordinated by Technische Universität Darmstadt (Germany) and has the participation of the following partners besides LNEC (Portugal): Institute of Communications and Computer Systems (Greece), Empresa de Transformación Agraria S.A. (TRAGSA) (Spain), Universitat Politècnica de Catalunya – BarcelonaTech (Spain) Studio Galli Ingegneria Spa (Italy), Scuola Superiore di Studi Universitari e di Perfezionamento Sant'Anna (Italy), Mekorot Israel National Water Company (Israel), Malta Resources Authority (Malta), EPEM S.A. - Environmental Planning, Engineering & Management (Greece), Etaireia Ydreyseos kai Apochetefseos Proteyoysis Anonimi Etaireia (Greece), Rheinisch-Westfälisches Institut für Wasserforschung (IWW) gGmbH (Germany), Helmholtz-Zentrum für Umweltforschung GmbH (Germany), Universidade do Algarve (Portugal), Terra, Ambiente e Recursos Hídricos (TARH) (Portugal), Autorita di Bacino dei Fiumi Isonzo, Tagliamento, Livenza, Piave, Brenta-Bacchiglione (Italy), Provincia de Lucca (Italy), Agricultural Research Organization - Volcani Center (Israel), Water Services Corporation (Malta) and Paragon Europe (Malta).

In the context of this dissertation, the research developed is included in WP 4 that concerns the DEMO site of Algarve coordinated by LNEC, and WP 14 – Water Quality, coordinated by IWW. WP14 main objectives are the compilation of potential and measured anthropogenic contaminants in the various infiltrated water sources, analysis of degradation pathways and

toxicology of infiltrated compounds and products, study eco-toxicological and pathogens impact on ecology of aquatic systems perform and model soil-column experiments to predict long-term geochemical changes in the aquifers and analyse potential effects on human health. It's divided into seven tasks that include the study of (1) water constituents, (2) fate of pollutants, (3) accompanying column experiments, (4) risk assessment, (5) model calibration with analysis of the potential of existing models, (6) model or combination of models selector and (7) water quality guidelines. The final results will be the development of guidelines for water quality requirements of source water in various MAR schemes.

## 1.2. Dissertation structure

Besides this introductory section this dissertation is divided in six other sections:

Section 2 synthetises a brief literature review on the main processes on MAR and explains the objectives of SAT processes. In Section 2 a special attention is given to the problem of emerging contaminants in the environment in particular in water, presenting a set of actual concerns and describing other projects that address this issue.

Section 3 describes the geological and hydrogeological background of the study area, as well as the main problems resulting from the discharge of wastewater and the possible use of this water supply in MAR processes by insuring that environmental conditions are enhanced by use of SAT.

Section 4 is the core of this dissertation and thoroughfully describes the laboratorial apparatus for all the experiments conducted for soil characterization, short and long term hydraulic behaviour, parameters analysed and both water and soil sampling procedures. In this section there is also the presentation of the methodologies and criteria used for the creation of soil mixture, an extensive description of the results achieved in soil characterization experiments, soil-column experiments and batch experiments conducted both in natural soil and soil mixtures.

Section 5 presents the numerical modelling processes at soil-column scale. A brief description of the software used is presented, as well as input data for column models. Output information concerning compound transport is summarized, as well as water speciation and inverse solution in geochemistry.

Section 6 compares Section 4 laboratory experiment results between natural soil and soil mixtures in terms of hydraulic behaviour and contaminant retention, allowing for the selection of the most suitable reactive layer.

Finally, Section 7 summarizes the main conclusions of this dissertation offering a set of recommendations concerning the reactive layer creation and operation procedures. Experiments limitations are also briefly discussed and suggestions on future research are given.

## 1.3. Objectives

The main objective of the research developed is, in general terms, to improve the environment conditions in the wastewater discharge area by increasing quality using Managed Aquifer Recharge through the usage of Soil-Aquifer Treatment (SAT). These methodologies are presented as a reliable complementary water treatment process and a solution, not only for water scarcity, but also environmental problems.

The application/use of SAT techniques requires an advanced knowledge of the purification/decontamination capacities of the soil and aquifer media that will act as a filter. In this sense, several soil characterization and soil-column experiments were conducted in the groundwater laboratory located in the Hydraulics and Environment Department of the National Laboratory for Civil Engineering (LASUB – **LA**boratório de Águas **SUB**terrâneas) in soils collected in the area of the infiltration basin installation. The objective of these experiments was to characterize the soil behaviour at lab scale but in similar conditions to those of infiltration scale. Also, simple batch experiments were conducted to define the maximum retention capacity of a set of pre-selected contaminants.

Depending on the results obtained, both in contaminant retention capacity – mainly by the comparison between the inflow and outflow parameters concentration – and by the hydraulic behaviour, a soil mixture can be produced and again tested in the soil-column experiments and batch experiments. The objective of this soil mixture is to increase the soil capacity to retain certain contaminants analysed in the inflow water, but also keeping hydraulic conductivity that allows an easily infiltration process without hindering the water-soil interaction processes. This soil mixture will act as a reactive layer to be installed on the bottom of the infiltration basins. This procedure – real scale experiments – will not be conducted during the time of conclusion of this dissertation, but the information collected will be fundamental for this stage.

A second stage is to be carried, dedicated to the modelling of the transport and retention of contaminants at column scale by using the Hydrus-1D software and water speciation with PHREEQC. This will allow the visually understanding of these processes that occurs in the soil-column given certain soil and contaminant parameters.

In summary, this dissertation includes the following objectives:

- Characterization of the infiltration basin soil properties.
- Characterization of the physical and chemical behaviour of these soils as a filtrating and purifying layer, both under soil-column and batch experiments conditions.
- Criteria definition, given the results obtained in the experiments, of the soil mixture for contaminant retention capacity increase.
- Numerical modelling of the chemical processes that occur at soil-column scale and simulation of transport in saturated and unsaturated media.

Initially two areas were defined for the application of SAT-MAR methodologies – São Bartolomeu de Messines and Melides Lagoon. Due to the large amount of data gathered and the lack of time to analyse it taking into account MARSOL project deadlines, this dissertation focused only in one of the study areas, São Bartolomeu de Messines.

# 2. State of the Art

In this section a brief literature review will be presented regarding the main subjects of this dissertation. Section 2.1 focus on Managed Aquifer Recharge while Section 2.2 presents some important aspects of the Soil-Aquifer Treatment, the main methodology studied in this dissertation. The following sections refer to the main aspects, problems and advantages of these methods, namely clogging, water origin and quality, ending with a section dedicated to Emerging Contaminants (EC) problematic.

## 2.1. Managed Aquifer Recharge

In general terms, Dillon *et al.* (2009) defined Managed Aquifer Recharge (MAR) as the purposeful recharge of water to aquifers for subsequent recovery or environmental benefit, while Gale (2005) defines MAR as an intentional storage and treatment of water in aquifers.

The term of Artificial Recharge has been the most common expression in the past to describe these processes. However adverse connotation of the "artificial" term resulted in the abandonment of this expression to avoid hindering the public acceptance of these processes. The term enhanced recharge has also been suggested by the scientific community. It's also easier to distinguish between the natural process of rainfall water infiltration and the anthropogenic induced process recharge, defining it as a well-organized, effective and efficient project with specific objectives.

As described by the United States National Research Council (NRC, 1994) report on artificial recharge[1] the main purpose of this process is to replenish an aquifer by storing water underground in times of surplus to meet water demand in times of shortage through infiltration methods such as surface spreading, recharge wells or by altering the natural conditions. Besides this use, this processes can also control sea water intrusion in coastal aquifers and migrant contaminant plumes, land subsidence resulting from declining groundwater levels or maintain streams base flow. These benefits can also be extended to impediment of soil erosion by increase of infiltration. DINA-MAR (2010) inventoried other environmental applications of MAR as a result of the water table rise in the recovery of groundwater dependent ecosystems such as caves, wetlands, prairies and marshes. Other uses may be temperature control for industry procedures using the stable temperatures of subsurface or the use of saline aquifers for potable water storage (Murray *et al.,* 2007).

Accordingly to Gale (2005), the benefits of an effectively managed aquifer can be of relevance in (1) poverty reduction & livelihood stability, (2) economic and health risk reduction, (3) increased agricultural yields resulting from reliable irrigation, (4) increased economic returns, (5) distributive equity by more accessible water to everyone and (6) reduced vulnerability. In small communities MAR may represent a cheap and safe water supply which will be essential in semi-arid and arid areas, and has been a common practice for centuries in several techniques.

The human activities which enhance aquifer recharge can be put into three categories (Dillon *et al.*, 2009): (1) unintentional, which result from the deep seepage under irrigation areas or

[1] At the time of report publication "artificial recharge" was the commonly expression used to refer MAR.

leaks from water pipes, (2) unmanaged, that includes stormwater drainage wells and septic tank leach fields and (3) managed, through specific mechanisms/devices.

Gale (2005) defined 15 types of MAR device classification, to which DINA-MAR (2010) added 8 more (variations of irrigation systems that result in an increase of water return to the aquifer and MAR in urban areas techniques) – Table 1. Some of these system schemes are represented in Figure 1.

**Table 1 – List of MAR devices (adapted from DINA-MAR, 2010)**

| System | Type of device |
|---|---|
| Disperse | Infiltration ponds |
| | Infiltration channels |
| | Soil-aquifer treatment techniques |
| | Infiltration fields |
| | Recharging by irrigation channels |
| Channels | Retaining dykes and reservoirs |
| | Permeable dykes |
| | Diversions |
| | Bed scarification |
| | Sub-surface/subterranean dykes |
| | Perforated dykes |
| Well | Qanats (subterranean galleries) |
| | Open infiltration wells |
| | Deep wells and mini-probes |
| | Probes |
| | Dolines, collapses, etc. |
| | ASR/ASTR |
| Filtration | Filtration banks in riverbeds (RBF) |
| | Inter-dune filtration |
| | Subterranean irrigation |
| Rain | Unproductive rainwater capture |
| Sustainable drainage urban systems | Accidental conduction and sewerage recharge |
| | Sustainable Urban Drainage Systems |

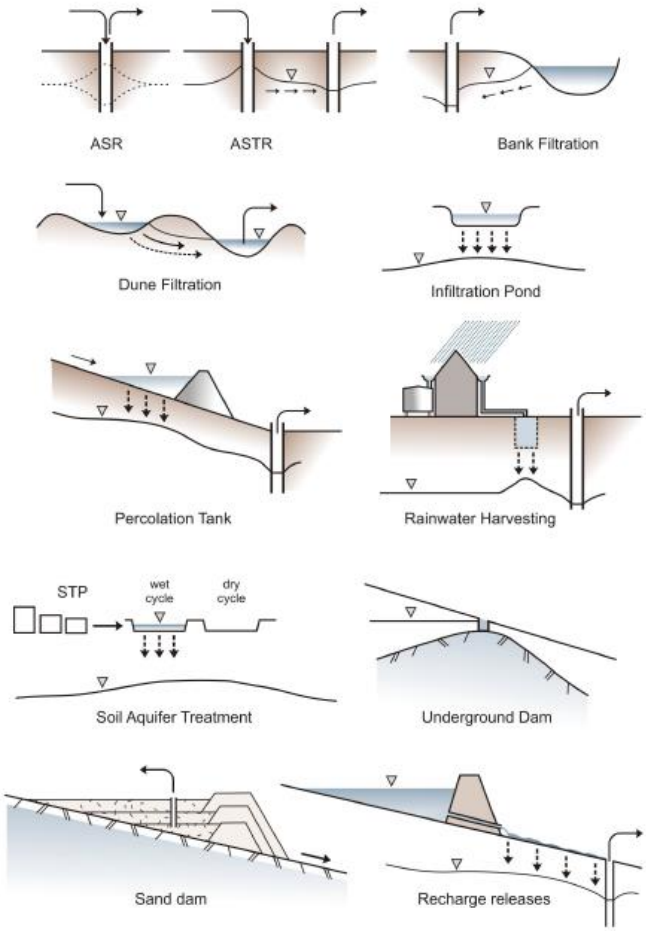



**Figure 1 – Different MAR schemes (adapted from Murray *et al.* 2007)**

These systems can be interconnected depending on the managing necessities, and can represent an integrated solution to surface/groundwater solution – Figure 2

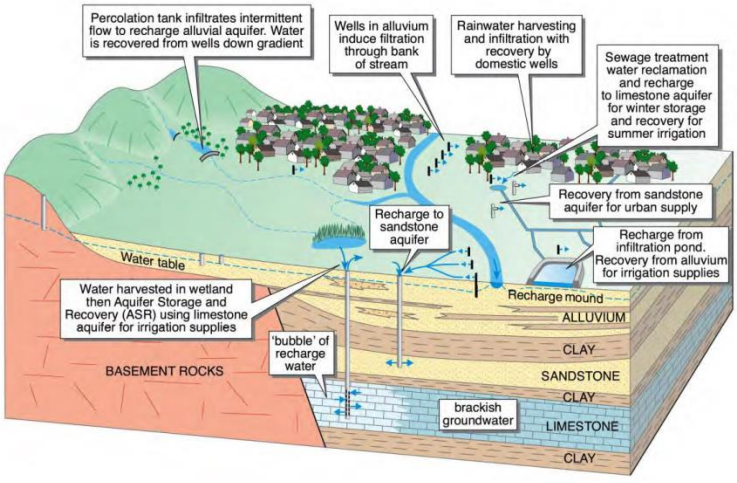



**Figure 2 – MAR (Dillon *et al.* 2009)**

As described by Dillon *et al.* (2009), the induced storage by MAR in aquifers has some advantages but also some disadvantages when compared to surface storing. The main advantage is the land area required which is very small compared with a surface dam. This represents an increase of area for rural and urban uses. MAR structures can be dimensioned accordingly to use, and they need considerably smaller surface areas when compared to dams that usually require a suitable valley, making it almost impossible to place them near urban areas. In the comparison of capital costs, a MAR structure is, by far, less expensive than a dam, and requires less investigation investment.

A surface reservoir is usually more exposed to evaporation losses, algal problems and mosquitoes and has a large contamination potential. In contrast, a below ground reservoir has a smaller supply rate and intake of water, but allows, by SAT processes, a natural decontamination. Also, as referred by Bouwer (2002) dams interfere with river ecology and can flood sensitive areas, with cultural, religious, archaeological, recreational and scenic impacts. Other advantages of aquifer storage is that the first doesn't need to relocate population, does not tend to have large silt accumulations, does not and produce large quantities of carbon dioxide and other greenhouse gases.

On the other hand MAR applications may require great expertise for it to be successful, which can represent an obstacle for its development. Also there is the concern about the possible damage of these processes in the aquifer and the environmental effects of the fluctuating groundwater levels, particularly in dependent ecosystems and, in shallow aquifers, the increase of aquifer vulnerability to contamination (Murray *et al.* 2010).These factors may be an obstacle at entry point for MAR implementation as a wide technique for managing groundwater, but so far it has been applied with success in several countries.

Dillon *et al.* (2009) defined five critical elements for a successful MAR project:

- Demand – within an economic scale, demand has to provide the revenue stream to pay for the water supply cost elements of a project. As an example in reclaimed water projects, the decline in discharge of treated effluent to sea may provide motivation for investment in MAR;
- Source – enough water for recharge must be available so it allows to build up a buffer storage to meet reliability and quality requirements;
- Aquifer – the media has to have enough storage capacity and be able to retain water;
- Detention Storage – there should be enough space for water detainment to enable the target volume of recharge to be achieved and also enough space for treatment process after recovery if necessary;
- Management capability – This means enough knowledge acquired both in hydrogeological and geotechnical and in terms of water storage and treatment design.

Several projects applied MAR methods with success. In Portugal, the 6$^{th}$ Framework Program GABARDINE project started in 2005, with the main objective of exploring the viability of supplementing existing water resources in semi-arid areas with alternative sources of water that could be exploited based on an integrated water resources management approach, tried to apply MAR technologies in the Southern region - Algarve. The main purpose of this application was to rehabilitate the groundwater quality of a heavily nitrate contaminated aquifer – Campina de Faro – resulting from several years of inappropriate intense agricultural uses (Diamantino, 2009). The water source used was from surface runoff and it was infiltrated into

basins built in the bed of a perennial stream. Other experiments using injection large diameter wells were also conducted in the area.

## 2.2. Soil-aquifer Treatment

It is well known that the natural water recycling happens through the global hydrological cycle, which is expected to suffer major variations due to the climatic changes. As anthropogenic pressures increase over water resources, it is important that a change in attitude towards water use occurs. It's in this context that the development of water reuse techniques is in implementation, being the growing research and application of Soil-aquifer Treatment (SAT) techniques a good example. Accordingly to Bouwer (2000), planned local water reuse may be important, as the discharge of sewage effluent is becoming increasingly difficult and expensive, since treatment requirements become more strict to protect the quality of the receiving waters, making economically attractive to treat and reuse rather than discharge.

Abel (2014) defines SAT as a land-based MAR technology adopted as a way to reliably enhance water resources and reduce indiscriminate discharge of treated wastewater to water bodies. Physical, chemical and biological processes improve the quality of wastewater effluent during infiltration through soil strata. Bdour *et al.* (2009) characterizes this process as a geo-purification system in which the aquifer is recharged with partially treated wastewater through the unsaturated zone before mixing with native water. In terms of methodologies, a treated effluent is intermittently placed in recharge basins, allowing for the infiltration into the ground for the recharge of the aquifers, and as the effluent moves through the soil and the aquifer it undergo quality improvement through the previously referred processes (Miotliński *et al.* 2010) - Figure 3.

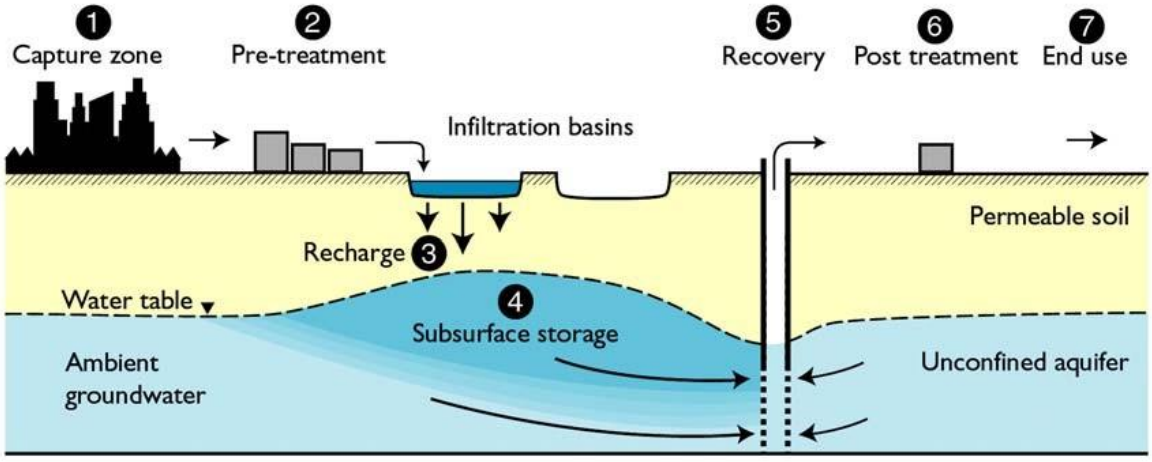



**Figure 3 – SAT system infiltrating water to an unconfined aquifer (Miotliński *et al.* 2010)**

The SAT process provides mechanical filtration of suspended particles and, resulting from intermittent aerobic and anaerobic conditions in the soil under the basin, nitrification and denitrification is facilitated, allowing the partial or total removal of organic and inorganic nitrogen and organic carbon, phosphorus, non-aromatic organic, trace metals or pathogens

(Miotliński *et al.*, 2010). The removal process can be controlled by managing wetting and drying cycles, and it's highly dependent on the quality of available water.

Simply put, NRC (1994) indicates that the soil and underlying aquifer have a great capacity to remove contaminants and pathogens, by reduction or removal of these constituents, as the water moves towards bigger depths in the aquifer. This represent an important step in reducing potential health risks at the time of recovery.

The pre-treatment of wastewater effluent can be made before spreading, to deliver the required quality either by regulations or for optimum operational purposes. SAT can be flexible concerning the wastewater quality and pre-treatment as primary, secondary or tertiary effluents can be used (Abel, 2014).

NRC (1994) determined that the ideal soil for SAT system balances the need for a high recharge rate (coarse-textured soils) with the need for efficient contaminant adsorption and removal (fine-textured soils). It should posess the suitable physical and chemical properties to achieve sufficient contaminant removal (Abel, 2014). For the stated reasons SAT systems are very site specific. Also wastewater effluent should be considered together with site characteristics to evaluate the feasibility of SAT (Cha *et al.*, 2004).

Abel (2014) studied the effects of several factors in SAT success of removal using primary effluent, such as effect of pre-treatment of primary effluent used, impact of hydraulic loading rate and soil type, wetting and drying cycles, biological activity and temperature and redox conditions. It was concluded that the pre-treatment of effluent alone resulted in 90% of suspended solids, 70% of dissolved organic carbon, 98% of phosphorous. Also, low hydraulic loading rates and fine particles soil can, with longer contact time and presence of adsorption processes, allow the reduction of nitrogen, while wetting/drying cycles helped in E. coli and total coliforms removal. Temperature and redox conditions also affect SAT performance, with high nitrogen removal at 15-25ºC temperature interval (89.7 to 99%) with an increase of nitrates and phosphates removal with temperature increase, indicating that lower viscosity increases adsorption. Higher contaminant removal was achieved with aerobic operating conditions, which suggested that aeration prior to infiltration process (with wetting and drying cycles) can improve SAT success. Malolo (2011) also showed temperature effect in ammonia nitrogen oxidation, which was maximum (76%) in soil-column experiments using primary effluent at temperatures of 20ºC. Phosphorous also shown a dependence on temperature.

Bekele *et al.* (2011) demonstrated that secondary treated wastewater was infiltration through a 9 m-thick calcareous vadose zone during a 39 month managed aquifer recharge (MAR) field trial resulted in the reductions of the average concentrations of phosphorous (30%), fluoride (66%), iron (62%) and total organic carbon (51%).

NRC (1994) also demonstrates the example of the nitrogen cycle in SAT in which nitrogen is quickly transformed to nitrates, very mobile in soils under normal conditions but can be removed by denitrification under anaerobic conditions. Other components such as phosphorus are reduced by sorption and precipitation, and trace metals, with exception of boron, are attenuated and can be precipitated in the soil, especially under alkaline and aerobic conditions.

SAT cannot substitute water treatment processes simply because processes by which removal occur are not completely efficient in natural settings, resulting from the significant number of ever changing factors, and not all constituents are retained or degraded. This is the

reason that NRC (1994) indicate that this processes is dependent on management strategies, and with adequate monitoring, a SAT system may help to reduce treatment costs.

Also, public acceptance of this type of treatment is fundamental for the implementation, and some communities still perceive recycled water as disgusting regardless to the extent of advanced water treatment the recycled water suffered (Abel, 2014). Socio-economic, cultural and religious factors can influence the use of this type of water, being education and community programmes fundamental to compete against false notions of unsafety and impurity (Bouwer, 1991). Many regions that face stress in their renewable source of water have not exploited this technology in full potential, so public outreach programs addressing these issues should be created to bridge the gap between institutions and end users (Abel, 2014).

Presently there are SAT facilities functioning worldwide. One example of successful application is Alice Springs SAT system, Australia. Operation started at 2008 and consists in four infiltration basins. As a result of this system operation Miotliński *et al.* (2010) observed that phosphorus removal is quite effective, and there is a freshening of the Quaternary aquifer with groundwater getting more suitable for agricultural purposes in terms of salinity which can be recovered in the future.

## 2.3. Clogging

As referred by Bouwer (2002), the main problem in infiltration MAR systems is clogging of the infiltrating surface that results in a decrease of infiltration rates. This phenomenon outcomes from physical, biological and chemical processes.

It's important, in the context of scaled laboratory experiments of MAR structures, to understand these processes as a way to comprehend the soil and aquifer behaviour, the effects of inflow water, and also to achieve the best conditions to avoid inviable projects.

Martin (2013) states that a MAR scheme will invariably experience clogging and where the selected method involves an injection and recovery bore (aquifer storage and recovery process or ASR, see Figure 1) the risk of clogging is potentially greater. In general, this process often results, in the case of infiltration basins, of minerals precipitation and gas entrapment in soil, biofilm formation and by algae and sediment accumulation and deposition. Hutchison *et al.* (2013) presents the effects of this phenomena in spreading facilities, such as reducing infiltration rates, diminishing the effectiveness of soil-aquifer treatment, necessity of regular maintenance (with basin flow ripping and draining) and in an extreme scenarios leading to site abandonment. Accordingly to Martin (2013), clogging can be divided into four types: (1) chemical, with elements precipitation and matrix dissolution, (2) physical that comprehend the suspended solids and interstitial fines migration, (3) mechanical such as entrained air binding and (4) biological with algae growth, iron or sulphate reducing bacteria.

The clogging layer in infiltration basins is usually not very thick (Hutchison *et al.*, 2013) and is composed essentially of suspended solids, algae, microbes, dust and salts. This layer will decrease permeability and make the basin bottom unsaturated. According to the author, two types of clogging layers exist: (1) upper layer with particulate matter, algae and/or microbes above the original sediment surface, and (2) lower layer composed with the native sediment with organic and inorganic solids trapped in the pore space.

In this type of structures, besides water quality, other parameters will influence the extent of clogging. One of the most relevant is the particle size of the soil media, where the fine grained sediments will create a clogging layer faster than coarse graded, although the extent of this layer may be bigger in coarse graded sediment media. Ponding depth is also a factor for clogging effect with a higher compaction of clogging layer occurring in higher depths. The loading rate (or rate at which water is applied to the soil surface) is also important to consider with lower hydraulic rates to achieve better results, especially in loading cycles where the basins are allowed to dry 50 percent of the time. Finally, vegetation in the pond will contribute to the decrease of soil permeability, considering not only root exudates but also effect from leafs. On the other hand root expansion may help in soil loosening (Hutchison *et al.*, 2013).

Concerning the chemical clogging, the main problems are related to the precipitation of iron oxides and hydroxides as well as calcium carbonate and usually are related to other forms of clogging. Accordingly to Martin (2013) many geochemical reactions are catalysed by bacteria, which creates a strong correlation to biological clogging, especially in iron and manganese rich aquifers and soils which, in the presence of oxygen, stimulate microorganisms the precipitate iron or manganese oxides and hydroxides. Dissolution is also a factor to instability, where soluble materials such as clays, anhydrite or halite may be dissolved leaving occluded pores that can be filled with insoluble fines creating blockage effects.

Physical clogging may have similar effects as chemical clogging. In spreading methods, fines migration associated with turbulence resulting from water injection pulses, can create fines settlement that be consequently suffer larger mobilization in each injection cycle. Concerning clays, swelling may be the biggest issue, which block pores and result in severe hydraulic conductivity reductions. Also, temperature variations may also affect infiltration due to the changes in water viscosity, which may be seasonal. Higher viscosity from lower temperatures results in lower infiltration rates. Benamar (2013) also concluded that physical clogging (as well as filtration) depends on particle concentration and flow conditions.

Biological clogging may result from growth of aerobic and anaerobic bacteria, usually from injection water and it’s directly associated with the amount of nutrients in solution, which accumulate themselves in biofilms that repel fluid and block pores.

Clogging problems can be prevented by controlling the injection water quality, by suspended solids removal, pH managing or dissolved oxygen control, although it does not solve microbiological activity clogging related problems. Also, extended ponding periods enhance soil clogging whereas wetting and drying cycles will ultimately help in reduce the effects of clogging layer (Hutchison *et al.*, 2013).

## 2.4. MAR water sources and quality

As stated by EU (2001), although the natural and artificial recharge involves basically the same physical, geochemical and biological processes, in the second case the infiltration rate is usually higher thus affecting the water content in the unsaturated zone. Also, depending on the origin, the concentrations of solute and contaminants in the water are higher when compared to rainwater, and most certainly will have different chemical composition from the aquifer water. In this scenario it’s important to have into account the chemical and microbiological impacts on the native groundwater.

The origin of water used in recharge processes can be diverse, from municipal wastewater, industrial wastewater, stormwater runoff and irrigation return flow. Gale (2005) extended the list of potential source of water for MAR, each with its own particularities in terms of quality: perennial stream/river/canal and intermittent flood flow, and storage dams.

Accordingly to NRC (1994) the injection water may be affected by several factors, directly dependent of its origin. For storm water runoff, besides its quantity and intensity, its quality is highly dependent on the characteristics of the drainage basin, time since last rainfall event and season. For irrigation return flow, that presents the widest variation in quality, may be dependent on the type of culture and the farmer irrigation methods, and this water source is not usually subjected to any kind of treatment.

In the case of wastewater, which represent a very interesting option given its immediate availability, its quality is related to the treatment processes that it has been subjected to – primary to tertiary treatment. The major constituents of this type of water are quite known, but less is known about trace constituents (see section 2.5). Also, besides organic compounds, nitrogen species, phosphorous and pathogen organisms, when water is treated to a higher degree, i.e. exposed to chlorine disinfection, the effluent will contain disinfection by-products which, in MAR, may represent a concern if the recovered water is for human consumption. Henze and Comeau (2008) divided the constituents of wastewater into main categories (Table 2).

**Table 2 – Constituents present in domestic wastewater (adapted from Henze and Comeau, 2008)**

| Wastewater constituents | | Effects |
|---|---|---|
| Microorganisms | Pathogenic bacteria, virus and worms eggs | Risk when bathing and eating shellfish |
| Biodegradable organic materials | Oxygen depletion in rivers, lakes and fjords | Fish death, odours |
| Other organic materials | Detergents, pesticides, fat, oil and grease, colouring, solvents, phenols, cyanide | Toxic effect, aesthetic inconveniences, bioaccumulation in the food chain |
| Nutrients | Nitrogen, phosphorus, ammonium | Eutrophication, oxygen depletion, toxic effect |
| Metals | Hg, Pb, Cd, Cr, Cu, Ni | Toxic effect, bioaccumulation |
| Other inorganic materials | Acids, for example hydrogen sulphide, bases | Corrosion, toxic effect |
| Thermal effects | Hot water | Changing living conditions for flora and fauna |
| Odour (and taste) | Hydrogen sulphide | Aesthetic inconveniences, toxic effect |
| Radioactivity | - | Toxic effect, accumulation |

Asano and Cotruvo (2004) refer four quality factors for reclaimed wastewater use in MAR: (1) microbiological quality, (2) total dissolved solids (TDS), (3) presence of heavy metal toxicants and (4) concentration of stable and potentially harmful organic substances. These factors will highly influence the pre-treatment and type of more suitable MAR, considering also its purpose, location and public acceptance, giving that the direct injection of wastewater into an aquifer, for later recovery, can require a more sophisticated approach in pre-treatment. A set of criteria for groundwater recharge with reclaimed wastewater has been proposed to the State of California Regional Water Quality Control Boards, which included total nitrogen requirement of 10 mg/L and 1 mg/L of nitrite.

Concerning the legislation framework, besides the Water Framework Directive (2000/60/EC) which defines the good chemical, quantitative and ecological status of water bodies, Groundwater Directive (2006/118/EC) that rules the groundwater chemical status concerning nitrates, pesticides and other parameters/compounds concentration, there is no official regulatory legislation to define the characteristics of source water to be used in MAR at European scale like the previous directives. The Water Framework Directive specifies MAR as measure to achieve acceptable status but without referring to quality aspects. National scale legislations start to take into account the MAR processes giving the importance of regulation in different water uses. According to DEMEAU (2013), several countries have regulated MAR having as background the European Framework. Spain, defined quality criteria for several parameters such as E. coli, TDS, turbidity, and nitrogen/nitrates. Netherlands Water Act integrates rules for artificial infiltration and protection of infiltration areas and soils, while Switzerland Federal law and Ordinance of water protection regulates MAR installations and defines the general requirements of groundwater quality affected by infiltration. Germany, in Groundwater Ordinance, defines values that refer to minimum water quality at the point of reaching groundwater surface. Previous projects such as AQUAREC (2006) or RECLAIMWATER (2012) suggested quality requirements for MAR injection water, which concern not only parameters like pH, conductivity and TDS but also nitrates, nitrites, ammonia, phosphate, sulphate, arsenic, boron, cadmium, chloride, chromium, zinc, mercury and lead.

## 2.5. Emerging contaminants

United States Environmental Protection Agency (EPA) defines emerging pollutants as new chemicals without regulatory status and which impact on environment and human health are poorly understood. Use of reclaimed or recycled water is more common nowadays not only in irrigation but also in MAR/SAT processes (and others that efficiently use this type of water). As usage of this source of water increases, the concept of emerging contaminants (EC) starts to be more of a concern, particularly in economically developed countries where environmental law tends to be more restrictive concerning water quality and the associated uses.

This results mainly from a more and more detailed view of these waters composition and its long term effects in the environment, particularly in the case of treated wastewater, due to the considerable organic and biologic content commonly found in some types of recycled water such as treated wastewater (Henze & Comeau, 2008).

The emergent contaminant problem, and in particular, the presence of pharmaceuticals in water is a more common subject nowadays mainly because of the recent advances in analytical chemistry and lower detection limits (Schwab *et al.*, 2005). Although, in the vast majority of cases, pharmaceuticals have been detected in natural waters only in nanograms to micrograms per litre, there is a lack of knowledge of their impact in the middle or long-term on human health as well as the environmental effects, particularly aquatic environments exposed to these compounds (Deblonde *et al.*, 2011).

These long term effects to are yet unknown, particularly those resulting from complex pharmaceutical mixtures, and there is an urgent need for risk assessment studies (Schwab *et al.*, 2005).

While not directly toxic or carcinogenic, the chemicals that enter wastewater by discharges of pharmaceutical industries, hospitals, medical facilities and households (by direct flushing and by human excreta with unmetabolized compounds) may produce adverse health effects by interfering with hormone production or by weakening immune systems (Bouwer 2000).

There are also records of problems in fauna and flora, namely an increase of bacteriological resistance to antibiotics and other compounds, increasing risk of disease as well as reproductive problems detected in aquatic organisms exposed to certain disrupting hormone compounds (Strathmann *et al.*, 2010). These are mainly a result of the direct discharge of pharmaceutical compounds in the environment through treated (or poorly treated) wastewaters and are recently being increasingly addressed in research programs.

For these reasons pharmaceuticals and similar compounds should be kept out of water environment as much as possible (NRC, 1994). Directive 2008/205/EC, which regulates the environmental quality standards of a set of priority hazardous substances in surface waters, does not contemplate the regulation of pharmaceuticals.

Christensen (1998) and Webb *et al.* (2003) conclude that concentrations found in aquatic media for some pharmaceuticals are subsequently transmitted to drinking water and to fish. However, these do not pose significant risk to human health although, accordingly to Cunningham *et al.* (2009), the effects of chronic exposure to the mixture of these emerging compounds should be prevented, possible susceptibility of individuals (particularly in debilitated or imunosupressed populations) should be defined, and the efficiency of treatment methods for the removal of pharmaceutical in wastewater treatment plants should be increased.

In a literature review by Calisto and Esteves (2009), large discrepancies are observed in the amount of pharmaceuticals removed during the treatment process of the WWTP, indicating that some employed methods show removal efficiencies below 10%, and consequently large quantities of active substances discharged unaltered. In some cases, this justifies a high occurrence of these compounds in environmental matrices, reinforcing the need to find viable alternatives to removal through remediation strategies that minimize the impact of this problem. With today's scientific knowledge, these low concentrations of pharmaceutical active compounds and other contaminants are, from a toxicological point of view, not harmful to humans but their occurrence in ground- or drinking water may not be desirable from a hygienic point of view or with regard to the precautionary principle (Heberer, 2002).

Richardson and Bowron (1985) addressed the problem of pharmaceuticals in aquatic environments, considering 200 of these substances. Many would metabolise to innocuous substances (conjugates) which can be hydrolysed during treatment. Biodegradation studies in 25 compounds that included naproxen, ibuprofen or paracetamol indicated that 14 of them were non-biodegradable (that included amitriptyline, chlorhexidine, clofibrate, coideine phosphate, dextropropoxyphene, erythromycin, meprobamate, methyldopa, metronidazole, naproxen, sulphamethoxazole, sulphasalazine, tetracycline and tulbutamide).

In a more detailed view, Ternes (1998), determined that due to the incomplete removal of drug residues during passage through a WWTP, above 80% of the 32 selected pharmaceuticals were detectable in at least one municipal sewage treatment plant effluent with concentration levels up to 6.3 mg/L (carbamazepine) and thus resulting in the contamination of the receiving

waters. It was also concluded that the drugs detected in the environment were predominantly applied in human medicine; therefore it can be assumed that the load of municipal WWTP effluents in the surface water highly influences the contamination - Figure 4.

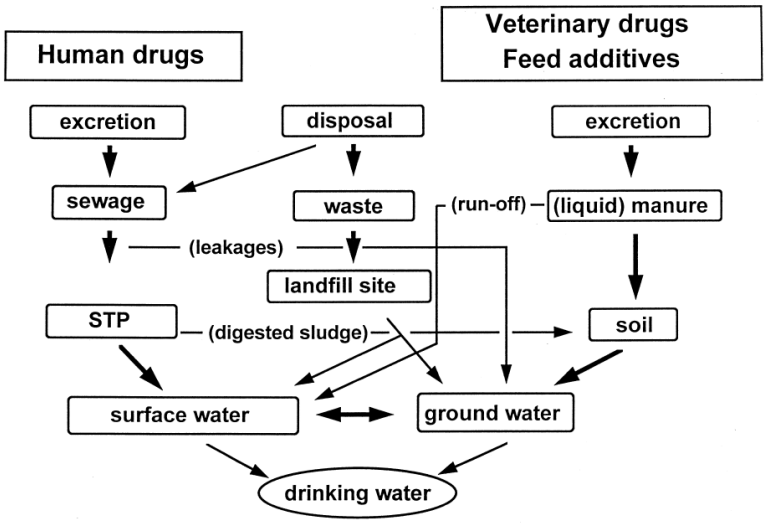



**Figure 4 - Scheme for the main fates of drugs in the environment after application (STP meaning sewage treatment plant) (adapted from Ternes, 1998)**

Heberer *et al.* (2011) concluded that several polar organic compounds, including pharmaceuticals, are relevant to MAR in bank-filtration (an efficient natural attenuation treatment process for natural surface-water). Compounds such as bezafibrate or, diclofenac seem to be removed effectively during bank filtration, while others, such as carbamazepine, clofibric-acid, primidone or propyphenazone are not (Lake Wannsee transect in Berlin, Germany). Endocrine disrupting compounds including herbicides and one pharmaceutical were also detected in surface water, water-supply wells, or drinking water at three bank-filtration sites in Nebraska, United States. Pharmaceuticals were also identified at the ng/L-level in Berlin tap water samples (Heberer, 2002).

Teijon *et al.* (2010) identified in Llobregat delta (Spain), 26 of 100 analysed compounds, where 22 of them were pharmaceuticals and 4 were personal care products (limit of recovery, LOR of 0.1 µg/L) in groundwater samples. Water from Depurbaix WWTP showed at effluent higher values than influent and diuretics, blood lipid regulator, beta-blockers, analgesics, antibiotics and fragrance where detected. In 60% of groundwater samples collected in that study area substances like caffeine, niconite and galaxolide (musk fragrance) were found, rarely exceeding a few µg/L. Carbamazepine, ibuprofen and sulfamethoxazone have also been found in WWTP and groundwater samples above LOR. Teijon *et al.* (2010) observed that from the set of compounds analysed, pharmaceuticals are the most common detected for that area. It was also observed that although tertiary treatment efficiently removed some compounds, others still been detected in much lower concentration.

In a database that included drugs for human health and disinfectants and collected concentration data for 50 pharmaceuticals, caffeine is the molecule whose concentration in influent was highest (in means 56.63 µg/L) with a removal rate around 97%, leading to a concentration in the effluent that did not exceed 1.77 µg/L. It was also shown that analgesics,

anti-inflammatories and beta-blockers are the most resistant to treatment with 30 to 40% of removal rate in WWTPs (Deblonde *et al.*, 2011).

Ying *et al.* (2004) detected the presence of endocrine disrupting compounds (EDC) in sewage effluents, such as 17beta-estradiol, 17alpha-ethynylestradiol, bisphenol A, in concentrations that range from nanograms to micrograms and conducted sorption tests to define attenuation factors in ASR systems. De Mes *et al.* (2005) defined EDC, used as oral contraceptives, as a threat affecting aquatic life by its estrogenic character, which environmental presence has been identified as a possible cause of adverse trends in reproductive health and prevalence of cancer in endocrine sensitive tissues

Although the issue of emerging contaminants is not likely to be, for now, a problem of major proportions, Jones *et al.* (2005) assert it would be prudent to apply in this case, the precautionary principle trying to reduce the levels of these compounds before their dangerousness is proven by monitoring and prevention.

DEMEAU project (7$^{th}$ Framework Programme), which aimed to demonstrate the importance of MAR concerning water quality impact and safety assurance, compiled a set of emerging substances and their removal rates influence parameters in several matrix. Accordingly to DEMEAU (2013) 12 pollutants from 40 compounds that represent emerging substances were selected considering a criteria: (1) commonly found in wastewater & drinking water supplies, (2) environmental relevance, (3) different chemical and physical properties, (4) cover the range from good to bad elimination by several methods and (5) existence of analytical methods of measuring its concentrations. These 12 substances (benzontriazole, bezafibrate, carbamazepine, epoxy-carbamazepine, diclofenac, gemfibrozil, iopromide, metroprolol, phenazone, primidone, sulfamethoxazole and trimethoprim) were analysed considering the influencing parameters that result in attenuation, like residence time (RT), redox conditions, organic carbon in sediment and water, attenuation/sorption capacity of sediment, and existence of an unsaturated zone and temperature.

From the literature review in DEMEAU (2015) it was learned that in MAR processes Benzotriazole compound removal occurs only in anoxic conditions with RT of 20 days to 1 year, with 75 to 85% of removal occurring in 4 months RT with iron/manganese reduction conditions. Bezafibrate attenuate in oxic to reductive conditions and RT ranging to days to 1 year. 40% removal achieved in nitrate reduction conditions and less than 3 months RT. Carbamazepine, which was found to be recalcitrant in both oxic and in nitrate and manganese conditions with pour removal, achieved rates of 99% removal in strictly anoxic conditions with long RT. Diclofenac removal occurred in different redox conditions and RT from days to months, being insignificantly removed under nitrate and manganese reduction conditions. Epoxy-Carbamazepine was removed (85%) in the presence of an organic layer at short RT, although the authors indicate that there is little information about this substance behaviour in MAR systems. Gemfibrozil is highly removed in all conditions and RT from 1 day to 3 months, with best rate achieved in high temperatures (97 to 100%). Ioprimide was successfully removed both in oxic and anoxic conditions with RT from 1 day to several months. Metoprolol shows high removal (100%) with long RT of more than 6 moths. Again, little information was collected about this substance. Phenazone showed good removal with short residence time and best results in oxic conditions (91%), although in some cases authors found inconsistent behaviour. Primidone was not removed in both oxic and reduction conditions and showed recalcitrant behaviour with only 30% removal in long RT. Sulfamethoxazole removal showed

good removal rates from 80 to 99% in anoxic conditions. Finally, from the 12 selected substances, trimethoprim removal was achieved both in oxic and anoxic conditions and RT ranging to 1 year, and high success achieved (90 to 100%) with 1 month of RT. In general, literature review showed consistency on the attenuation conditions of each compound.

In this context the authors defined a set of design and planning instructions for the removal of these substances, concerning the potential additional water and soil treatment to ensure attenuations – Table 3.

**Table 3 – DEMEAU MAR operation instructions (adapted from DEMEAU, 2013)**

| Compound | Aquifer conditions |
|---|---|
| Benzotriazole | In nitrate and iron-manganese reducing conditions and with residence time between 3 and 12 months the maximum expected natural removal is between 50 and 90% |
| Bezafibrate | All aquifer conditions ensure > 90% removal |
| Carbamazepine | Removal rates >90% are only expected in aquifer with very long residence time (at least 6 months) and anaerobic conditions (sulphate reducing conditions) |
| Diclofenac | All aquifer conditions ensure >90% removal except more reducing conditions where the removal is above 50% |
| Epoxy-carbamazepine | Not enough information to identify removal conditions |
| Gemfibrozil | All aquifer conditions ensure >90% removal |
| Iopromide | All aquifer conditions ensure >90% removal |
| Metoprolol | Not enough information to identify removal conditions |
| Phenazone | Phenazone reaches 100% removal rates in oxic to slight anoxic conditions and short residence times |
| Primidone | It is not removed at any aquifer conditions |
| Sulfamethoxazole | Removal rates >90% are only expected in aquifer with very long residence time (at least 6 months) and anaerobic conditions or strictly anaerobic conditions (sulphate redox conditions) |
| Trimethoprim | All aquifer conditions ensure >90% removal |

Concerning experiments directly correlated with SAT and removal of these substances, Abel (2014) concluded using soil-column experiments that phenacetin, paracetamol, ibuprofen and caffeine were easily removed under various operating conditions. Also, increased biological activity allowed for a substantial removal of gemfibrozil, diclofenac, pentoxifylline and bezafibrate from the primary effluent used, for periods of 240 days.

Mansell *et al.* (2004), in soil-column experiments on silica sand showed that adsorption is the primary mechanism of removal for 17β-estradiol, estriol, and testosterone hormones studied, with removals of 79.3 ± 2.4%, 84.3 ± 14.6%, and 97.5 ± 1.7%, respectively. It was also observed that removal efficiencies were higher on soil containing a higher content of silt, clay and organic content, demonstrating that SAT is efficient in removing hormones present in reclaimed water.

At infiltration basin scale, Life+ ENSAT project, tried to demonstrate the efficiency of a vegetal compost-made reactive organic layer. After a set of laboratory experiments this layer was applied at a full scale MAR system, where several pollutants reduction, usually present in recharge water, where taken into account to verify the suitability of the referred reactive layer

(ENSAT, 2012a). The project focused on recalcitrant compounds that resist to advanced treatment processes – organic micro pollutants. By adding organic matter to the reactive layer mixed with original soil (Figure 5) installed at the bottom of the pond, biodegradation as well as adsorption processes can be enhanced.

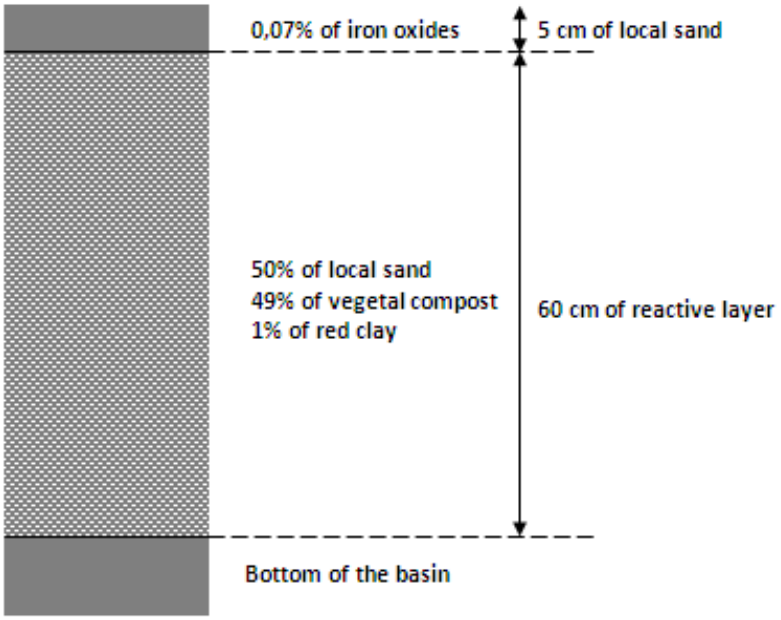



**Figure 5 – Scheme of the reactive layer (adapted from ENSAT (2012b))**

Thirteen compounds where selected, including degradation products (8 pharmaceuticals, 4 pesticides and 1 estrogenic compound) and some of them where in Directive 2008/105/EC. The substances and the effects suffered by application of a reactive layer are shown in Table 4.

Aqueous behaviour of these substances is highly dependent on their physicochemical properties, such as molecular weight, octanol-water partition coefficients, solubility and acid dissociation constant. These are key parameters to take into account when considering treatment (Caballero, 2010). Octanol-water partition coefficient ($K_{ow}$) describesthehydrophobic ($K_{ow}$>2) or hydrophilic ($K_{ow}$<2) character of a given compound. This important property allows anticipating the tendency of a compound to adsorb onto suspended solids and sediment during infiltration. Hydrophilic compounds remains in aqueous phase due to its affinity with water.

Acid dissociation constant (Ka) gives a measure of ability of an acid to donate protons to a respective base, the greater this values are the stronger the acid in the solution. These two parameters together are can give efficient information for estimating the fate of a compound in a system.

**Table 4 – ENSAT substances and results summary (adapted from ENSAT, 2012)**

| Compound | | Use | Result |
|---|---|---|---|
| **Pharmaceuticals** | Atenolol | Beta-blocker | Not found in recharge water |
| | Carbamazepine | Psychotropic | No effect observed |

| Compound | | Use | Result |
|---|---|---|---|
| | Carbamazepine-epoxy | Transformation product | Reduction observed by reactive layer effect |
| | Diclofenac | Non-steroidal anti-inflammatory | Not found in recharge water |
| | Gemfibrozil | Lipid regulator | Reduction observed by reactive layer effect |
| | Ibuprofen | Analgesic, anti-inflammatory | Not found in recharge water |
| | Ibuprofen hydroxyl | Transformation product | Not found in recharge water |
| | Sulphametoxazol | Antibiotic | Not found in recharge water |
| **Pesticides** | Diuron | Herbicide (phenyl urea) | No effect observed |
| | DIA | Transformation product | Not found in recharge water |
| | Simazine | Herbicide (triazine) | No effect observed |
| | Simazine hydroxyl | Transformation product | No effect observed |
| **Estrone** | Estrone | Estrogenic hormone | Not found in recharge water |

DEMEAU (2013) compiled information about the behaviour of some organic pollutants and also solubility and mobility information – Table 5. For example, carbamazepine can be retarded in the presence of soil organic matter based on laboratory results but field data seems to relate the removal with dilution processes. Retardation is governed by carbamazepine desorption kinetics from adsorbing sites. Ibuprofen is significantly retarded and biodegraded while diclofenac has a higher transformation in unsaturated conditions rather than under saturated conditions.

**Table 5 – Solubility and mobility information of a set of selected organic compounds (adapted from DEMEAU, 2013) (Ka –acid-base dissociation constant; $K_{ow}$ – octanol water distribution coefficient)**

| | Ka | $K_{ow}$ (ph=7) | $K_{ow}$ |
|---|---|---|---|
| Bezafibrate | 6 | 0.85 | 4.25 |
| Carbamazepine | 13.93 | 2.4 - 2.63 | 2.45 - 2.67 |
| Diclofenac | 4.15 | 1.65 - 1.06 | 4.06 |
| Gemfibrozil | 4.8 | 2.19 | 4.39 |
| Metoprolol | 9.6 | -0.8 | 1.9 |
| Primidone | 12.3 | 0.4 | 0.4 - -0.84 |
| Sulfamethoxazole | 5.7 | -0.43 | 0.89 |
| Trimethoprim | 6.6 | 0.51 | 0.91 |

All collected information may be useful for understanding behaviour of these contaminants, although much is yet unknown about the reactions that occur in the degradation and retention processes.

# 3. Study area characterization: São Bartolomeu de Messines

In this section a general characterization of the study area will be presented, addressing regional geology to hydrogeological factors, water quality and some socioeconomic facts.

## 3.1. Global characterization

The study area is located in the northern limit of Querença – Silves aquifer system, situated in the Algarve region, south of Portugal (Figure 6). Geologically, this system is a karstic multi-aquifer, with confined to unconfined layers, limited in the northern contact by Grés de Silves (sandstone) formation and, in the south, by Jurassic Callovian-Oxfordian-Kimmeridgian limestones and marls where the aquifer geological formations can have 270 m of thickness. Karstification is observed and is only developed to smaller depths, which locally can achieve 200 m. This aquifer system has a complex geometry, reflected in the pattern of the surfacing geologic formations, resulting from the tectonic activity that compartmentalized the aquifer system in smaller subsystems with hydraulic connections between them that vary in rate of groundwater transferral (Almeida *et al.*, 2000).

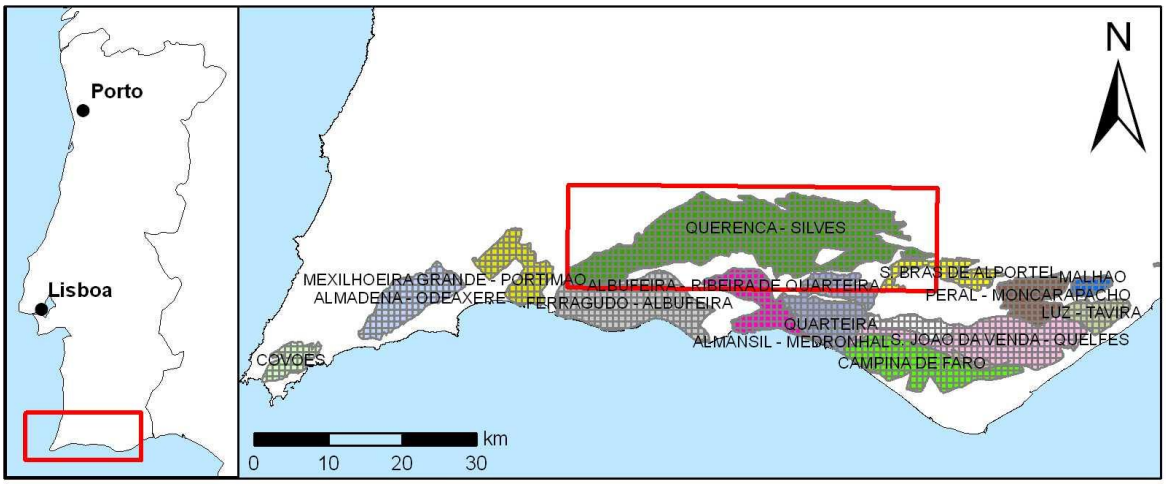



**Figure 6 – Location of Querença-Silves aquifer system**

Monteiro *et al.* (2006), Monteiro *et al.* (2007) and Reis *et al.* (2007) refer that, besides this complexity in the subsurface media, there is transference between subsystems induced by streams, that transfer water from the upstream subsystems to downstream subsystems by a succession of springs and areas of infiltration in the stream beds. Water flow does not occur exclusively underground, but there is also a superficial component of circulation and hydraulic connection between different sectors of the aquifer system. It's possible to conclude that complex surface/groundwater relations are established, where streams (seasonal or not) frequently represent the hydraulic connection between sectors (or subsystems) that otherwise would function independently. Figure 7 represents the distribution of receptor (influent) and donator (effluent) sections of the main streams that pass through the aquifer.

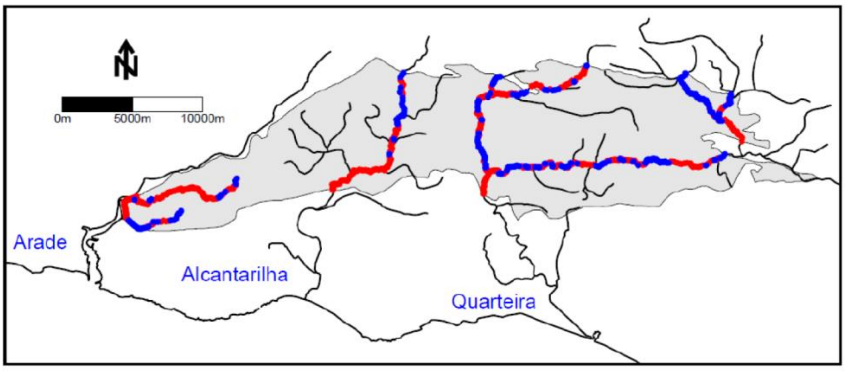



**Figure 7 – Influent (blue) and effluent (red) sections of the streams that pass through Querença – Silves aquifer system (adapted from Monteiro *et al.*, 2006).**

The study area is situated near the zone of influence of Ribeiro Meirinho, a tributary of Alcantarilha stream. This stream upper reaches are located outside the aquifer, in Serra Algarvia and flows south throughout the central-western area of Querença-Silves aquifer. Serra Algarvia are Palaeozoic terrains, composed essentially by impervious lithologies, being the main source of water for this stream until it reaches the Jurassic calcareous formations composing the karst aquifer of Querença-Silves (Leitão *et al.*, 2014).

Reis *et al.* (2007) refers an influent behaviour in the upstream section of Ribeiro Meirinho and an effluent behaviour in the downstream area, where it suffers a severe flow reduction when it reaches the karstic formations, having several sinks located along its riverbed. Ribeiro Meirinho has no significant flow during most of the year and its watershed upstream from the northern limit of the aquifer system is of small dimension. This stream acts as an hydraulic passage and transfers water received from northern Palaeozoic formations by surface flow and/or possible subsurface flow from them to the aquifer system.

Water availability in the region is low, and therefore, the importance of its preservation is clear (Leitão *et al.*, 2014). The average annual recharge of Querença-Silves aquifer, for the period 1941–1991, was estimated as 314 mm/year (Oliveira *et al.*, 2008) and 294 mm/year for the period 1979–2009 (Oliveira 2011).

## 3.2. Local characterization: SBM Wastewater treatment plant

Considering the global characteristics referred in the previous section and the significant importance of the groundwater/surface water relations in the aquifer system, a set of infiltration basins was purposed for construction to improve the aquifer recharge that occurs naturally through Ribeiro Meirinho (Lobo Ferreira *et al.* 2013) by using the treated effluent from São Bartolomeu de Messines Wastewater Treatment Plant (WWTP) in the upstream section of the aquifer system – Figure 8. This generally aims to increase availability by storing excess water in Querença-Silves aquifer during wet years, allowing for complementary response to the use of surface water reservoirs in case of long drought periods, assuring continuity in consumer supply.

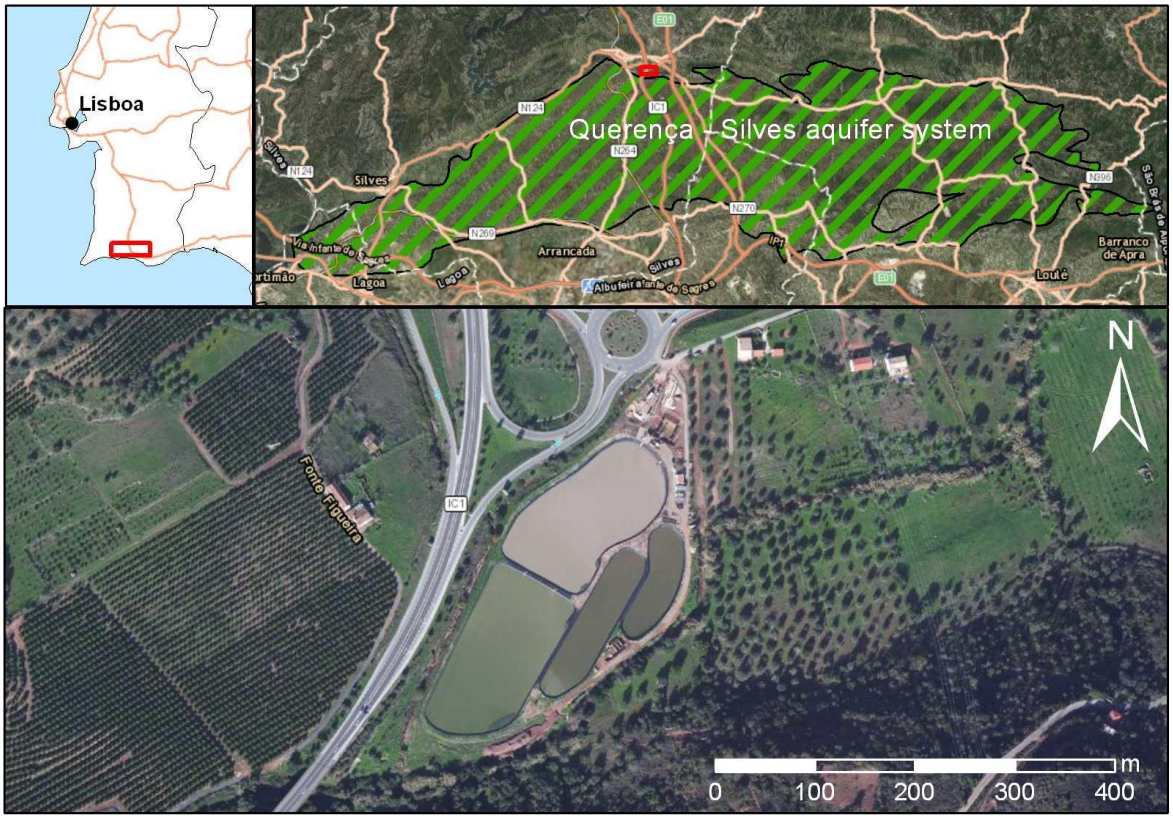



**Figure 8 – São Bartolomeu de Messines Wastewater Treatment Plant location**

São Bartolomeu de Messines Wastewater Treatment Plant (SBM WWTP) treated effluent is directly discharged to Ribeiro Meirinho. The objective of the infiltration basins is to improve wastewater quality through SAT processes, acting as a complementary treatment process.

SBM WWTP is managed by Águas do Algarve (AdA), a Portuguese public enterprise, and was previously managed by local authority of Silves municipality. It receives mainly urban effluent for treatment from São Bartolomeu de Messines and serves an average of 4228 inhabitants. The volume of wastewater treated is about 316891 $m^3$/y (AdA and ERSAR, 2008).

This infrastructure has secondary treatment and a disinfection process by ultraviolet radiation (UV) – Figure 9. UV disinfection (a good alternative to chemical disinfection), basically inactivates bacteria and viruses by exposing microorganisms to electromagnetic radiation that disrupts its genetic material and interferes with reproduction process (NRC, 1994). This process allows for the disinfection by-products resulting from transformation of chemical disinfection products to be greatly reduced.


**Figure 9 – SBM WWTP UV treatment infrastructure**

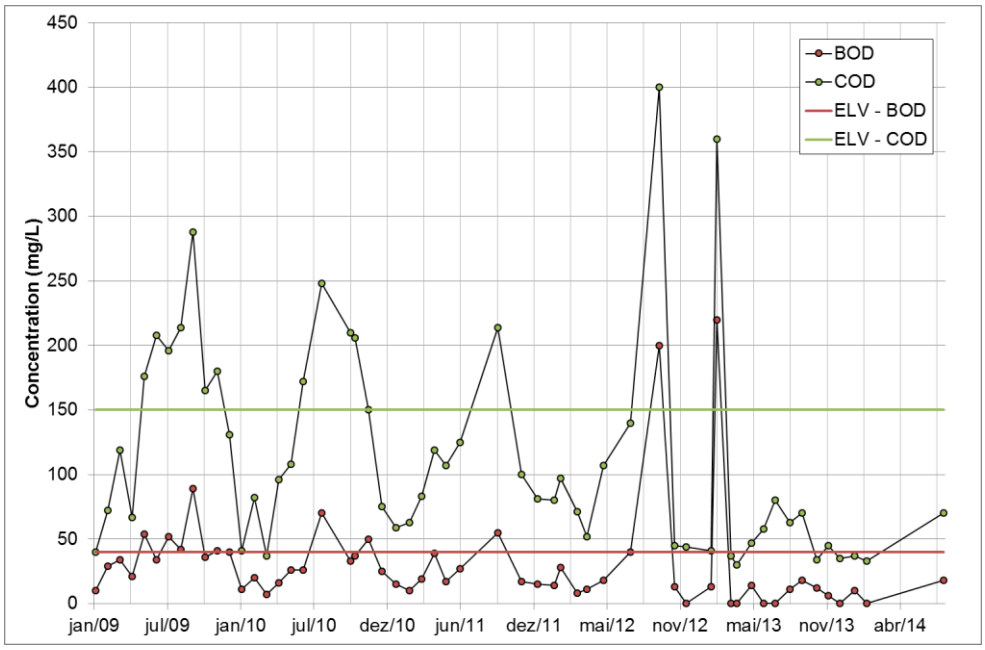
After treatment, the water is directly discharged to Ribeiro Meirinho stream – Figure 10.


**Figure 10 – Point of discharge of SBM WWTP to Ribeiro Meirinho stream (blue line on the map)**

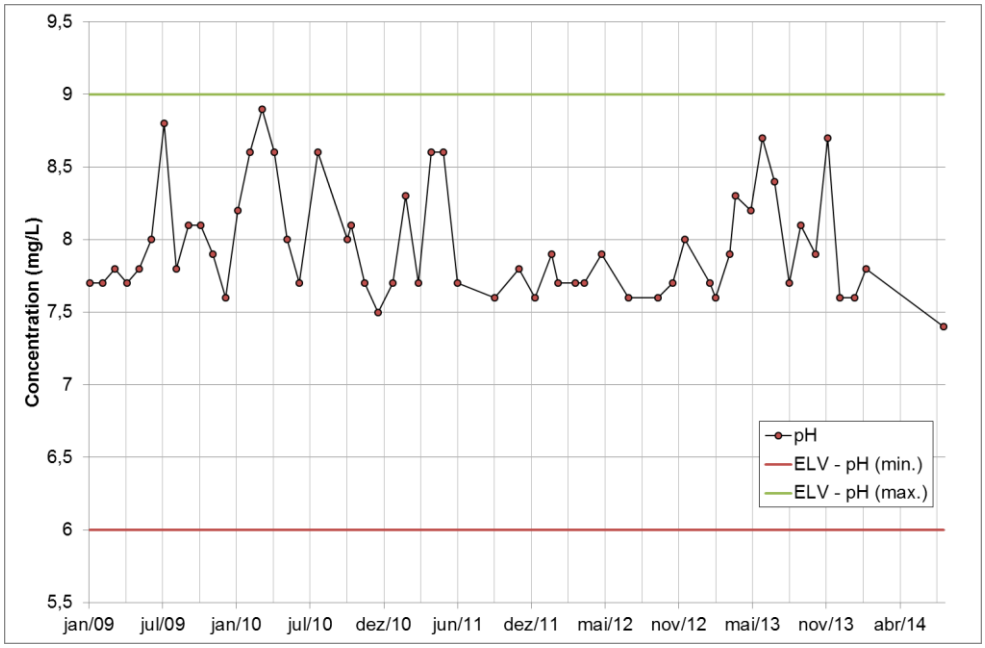
Concerning water quality, this effluent shows expected variability. Data is from Águas do Algarve (AdA) from effluent monitoring, which control several parameters such as pH, COD, BOD, phosphates, nitrogen, chloride and E. coli, is frequently published. Graph 1 to Graph 4 shows parameter concentration for the period of 2009 to 2014 for samples collected at point of discharge. Values are compared to the maximum acceptable concentrations for wastewater at discharge established (emission limit values - ELV) in Legislative Decree 236/98, except for Total Coliforms which reference value corresponds to maximum recommended value (MRV) for drinking waters.

In Appendix 1 is the table showing the parameter concentrations for samples collected at point of discharge published by Águas do Algarve.

From the collected data it's possible to observe at Graph 1 that BOD and COD concentrations are often above the ELV, mainly during summer months, while Graph 2 shows that pH values for the considered period respects the ELV interval (6 to 9), without showing evidence of seasonal pattern.

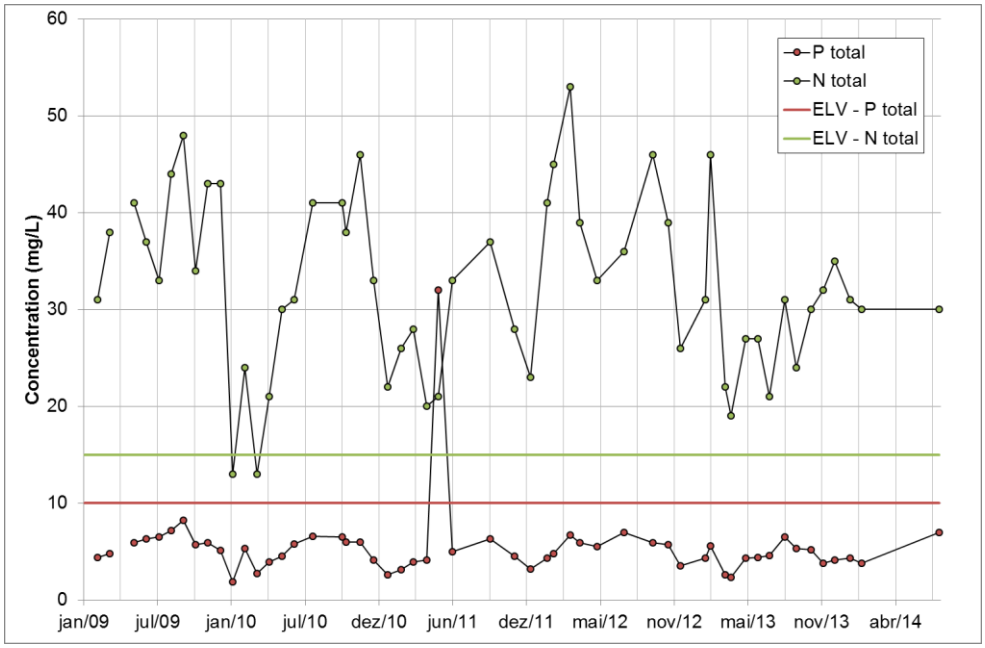



**Graph 1 – BOD and COD concentration at SBM WWTP point of discharge**



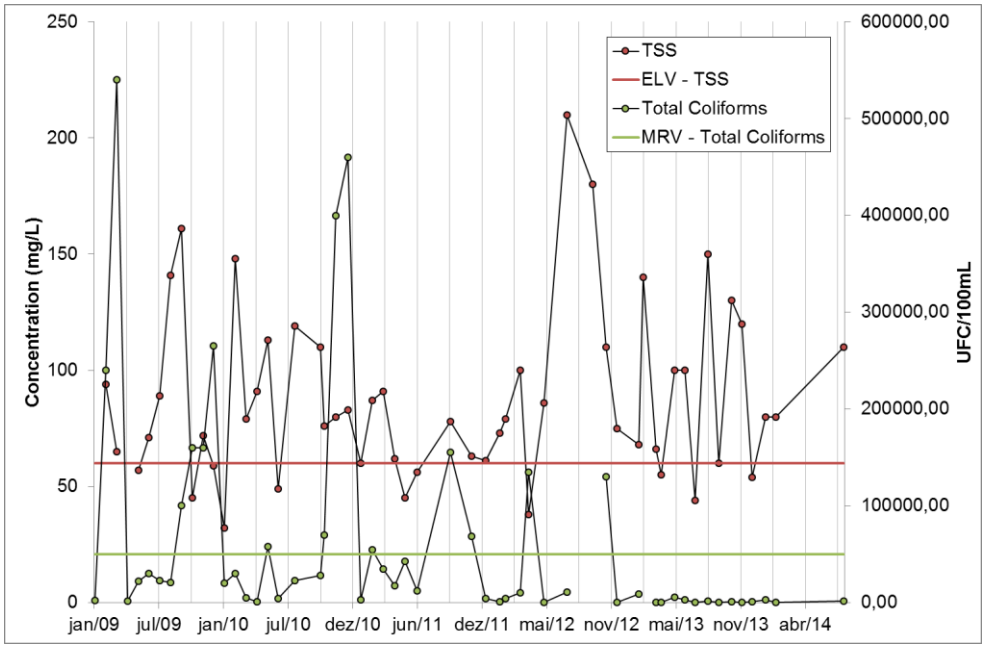

**Graph 2 – pH at SBM WWTP point of discharge**

Graph 3 shows that N total is often above ELV at SBM WWTP point of discharge, with an evidence of seasonal effects with higher concentrations in the summer months, except for the year of 2013. P total show values below ELV except for March 2011.




**Graph 3 – Total nitrogen and phosphorous concentrations at SBM WWTP point of discharge**

Finally, Graph 4 presents the Total Coliforms (TC) and Total Suspended Solids. While the first parameter (TC) presents a concentration higher than MRV for certain periods of the year, it is very clear that TSS does not respect the ELV in most of the samples at point of discharge.




**Graph 4 – Total suspended solids and total coliforms at SBM WWTP point of discharge**

This WWTP shows, for the selected period of available data some problems in the effluent treatment. Note that a comparison between the WWTP affluent and effluent parameter concentrations for the determination of elimination percentage is not possible due to affluent parameters concentration not being available. The Legislative Decree 152/97 refers that this comparison is to taken into account when determining the quality of effluent at discharge point. Also there is no available/published information for metals, total hydrocarbons or detergents, which are also referred in Legislative Decree 236/98 as control parameters for the effluent quality.

Considering the type of effluent treated in São Bartolomeu de Messines WWTP, which is mainly urban, pharmaceuticals were considered in this study. As reported in Section 2.5, this type of contaminants is commonly found in wastewater. To understand, the extent of the problem in a small population, several wastewater analysis where conducted in different field campaigns in different conditions. Pharmaceuticals and other emergent substances are not monitored by Águas do Algarve.

The first campaign was led in May of 2014, and several parameters where measured, including pharmaceuticals – Table 6. Sample analyses were conducted in an external laboratory and the measured pharmaceuticals correspond to a fixed set of compounds and where not pre-selected which include several types of these substances, from anti-inflammatory to hormones. The remaining parameters measured were determined accordingly to Section 4.2.3 set of parameters considered and common in wastewater.

**Table 6 – May 2014 campaign results**

| Parameter | Units | Limit of Recovery (LOR) | Conc. | Parameter | Units | Limit of Recovery (LOR) | Conc. |
|---|---|---|---|---|---|---|---|
| Ammonia ($NH_4$) | mg/L | 0,05 | **17,3** | **Clofibrate** | µg/L | 0,02 | <0,02 |
| Nitrates | mg/L | 0,27 | <0,27 | **Caffeine** | µg/L | 0,02 | **0,14** |
| Nitrites | mg/L | 0,005 | **0,0269** | **Lincomycin** | µg/L | 0,01 | <0,01 |
| Sulphate ($SO_4^{2-}$) | mg/L | 5 | **35,4** | **Metoprolol** | µg/L | 0,06 | <0,06 |
| Boron | mg/L | 0,01 | **0,059** | **Monensin** | µg/L | 0,01 | <0,01 |
| Copper | mg/L | 0,001 | **0,0072** | **Oleandomycin** | µg/L | 0,02 | <0,02 |
| Zinc | mg/L | 0,002 | **0,055** | **Pentoxyfillin** | µg/L | 0,01 | <0,01 |
| **Aminopyrine** | µg/L | 0,05 | <0,05 | **Primidone** | µg/L | 0,04 | <0,04 |
| **Cyclophosphamide** | µg/L | 0,01 | <0,01 | **Progesterone** | µg/L | 0,01 | <0,01 |
| **Dapsone** | µg/L | 0,05 | <0,05 | **Propranolol** | µg/L | 0,01 | <0,01 |
| **Erythromycin** | µg/L | 0,01 | <0,01 | **Roxithromycin** | µg/L | 0,01 | <0,01 |
| **Ethinyl estradiol EE2** | µg/L | 0,5 | <0,50 | **Spiramycin** | µg/L | 0,05 | <0,05 |
| **Phenazone** | µg/L | 0,01 | <0,01 | **Sulphadimidine** | µg/L | 0,05 | <0,05 |
| **Fenofibrate** | µg/L | 0,01 | <0,01 | **Tiamulin** | µg/L | 0,01 | <0,01 |
| **Fenoterol** | ng/l | 0,02 | <0,02 | **Trimethoprim** | µg/L | 0,02 | <0,02 |
| **Carbamazepine** | µg/L | 0,02 | **0,33** | **Estrone** | ng/l | 0,1 | <0,10 |

Note: parameters in bold represent pharmaceuticals; concentrations in bold represent values above LOR; Conc. – concentration

From the set of 32 parameters analysed in SBM WWTP effluent, only 8 where above LOR. Low values of nitrates, boron copper and zinc where detected and relatively high concentrations of sulphate and ammonia where measured. Concerning the pharmaceuticals only carbamazepine and caffeine where detected. The presence of these substances is coherent with what was presented in Section 2.5, especially with carbamazepine which shows small reduction after treatment and has a persistent behaviour.

A second campaign was conducted in the end of September 2014 where data from the affluent was also collected. Again the set of pharmaceuticals considered in the analysis was defined by default in the external laboratory – 84 pharmaceuticals where considered in the effluent analysis. A new set of parameters were also considered, such as chloride, dissolved organic carbon (DOC), iron, potassium, magnesium, manganese, sodium, nickel, total phosphates, total phosphorous, cadmium, calcium, total hardness, total alkaline earth, arsenic, lead, chemical oxygen demand (COD), biological oxygen demand (BOD) and total soluble solids (TSS).

**Table 7 – September 2014 campaign results**

| Parameter | Units | Concentration | |
|---|---|---|---|
| | | Effluent in | Effluent out |
| Electrical conductiviy | µS/cm | **969** | **979** |
| Ammonia | mg/L | **26** | **23** |
| Nitrite | mg/L | **0.2** | **0.16** |
| Chloride | mg/L | **113** | **99.8** |
| Nitrate | mg/L | <1.00 | <1.00 |
| Sulfate | mg/L | **63** | **11.3** |
| DOC | mg/L | **49** | **19** |
| Iron | mg/L | **0.12** | <0.100 |
| Potassium | mg/L | **15** | **17** |
| Copper | mg/L | <0.010 | <0.010 |
| Magnesium | mg/L | **17** | **18** |
| Manganese | mg/L | **0.03** | **0.04** |
| Sodium | mg/L | **75** | **86** |
| Nickel | mg/L | <0.020 | <0.020 |
| Total phosphates | mg/L | **15** | **10** |
| Total phosphorous | mg/L | **4.8** | **3.3** |
| Cadmium | mg/L | <0.0020 | <0.0020 |
| Calcium | mg/L | **24** | **31** |
| Total hardness | °dH | **7.28** | **8.49** |
| Total alkaline earths | mmol/L | **1.3** | **1.51** |
| Arsenic | mg/L | <0.0010 | <0.0010 |

| Parameter | Units | Concentration | |
|---|---|---|---|
| | | Effluent in | Effluent out |
| Lead | mg/L | <0.001 | <0.001 |
| COD | mg/L | **320** | **150** |
| BOD | mg/L | **100** | **36** |
| TSS | mg/L | **148** | **58** |
| **Bisphenol A** | µg/L | NA | **0.09** |
| **4-tert-Octylphenol** | µg/L | NA | **0.04** |
| **Sulfamethoxazol** | µg/L | NA | **0.02** |
| **Trimethoprim** | µg/L | NA | **0.01** |
| **Atenolol** | µg/L | NA | **0.09** |
| **Bisoprolol** | µg/L | NA | **0.04** |
| **Metoprolol** | µg/L | NA | **0.04** |
| **Propanolol** | µg/L | NA | **0.03** |
| **Sotalol** | µg/L | NA | **0.07** |
| **Diclofenac** | µg/L | NA | **0.24** |
| **Naproxen** | µg/L | NA | **0.4** |
| **Carbamazepin** | µg/L | NA | **0.51** |
| **β-Sitosterol** | µg/L | NA | **10.6** |
| **Sodium Amidotrizoate** | µg/L | NA | **0.52** |
| **Iopromid** | µg/L | NA | **7** |
| **Sodium Ioxithalamin** | µg/L | NA | **0.06** |
| **EDTA** | µg/L | NA | **6.6** |

Note: parameters in bold represent pharmaceuticals with concentration above LOR; NA – Not analysed.

From the 25 parameters analysed in WWTP affluent, 19 showed values above LOR. In the treated effluent a total of 7 from 42 analysed parameters showed values below LOR. In pharmaceuticals, beta-sitosterol, iopromid and EDTA presented values of 10.6, 7 and 6.6 nanograms per litre, when others stayed below 1 nanogram per litre. In total, from the 84 pharmaceuticals considered, 17 where above LOR. COD and BOD concentrations seam coherent with published data from Águas do Algarve. Nitrogen elements show lower values than expected, considering the main stressors in the area (Leitão *et al.*, 2014).

Comparing WWTP inflow and outflow, ammonia, nitrite, chloride, sulphate, DOC, iron, magnesium, total phosphates and phosphorous, COD, BOD and TSS presented a reduction after treatment. Other parameters had the inverse behaviour with an increase of concentration on the outflow.

Appendix 2 presents all measured pharmaceuticals in the campaigns. Note that in Section 4 other wastewater analysis results will be presented for SBM WWTP effluent, as this water was used in the laboratory soil-column and batch experiments.

This WWTP serves an aging population, where accordingly to INE (2011) 28% of the population is in the age group of >64 years old and 51.6% is in the age group of 25 to 64 years old. An aged population may be the main factor for the presence of unmetabolized pharmaceuticals in wastewater in this study area, where there is also a local healthcare unit. To date it is unknown if this units sewage is treated independently.

Also, Algarve see its population increase significantly during Summer season because of its warm weather, so there may be a seasonal factor in the presence of pharmaceuticals in wastewater.

# 4. Laboratory experiments

In this section, the laboratory experiments conducted are descript and the results are presented. In addition to the soil-column and batch experiments, soil granulometry, organic matter percentage, carbonate percentage, cation exchange capacity and clay type were also determined for the natural soil (results presented in section 4.3.1.1). Some parameters were also determined for soil mixture – results in section 4.3.2.1.

## 4.1. Soil characterization methods

Several experiments were conducted in LASUB for the determination of soil characteristics.

The granulometric characterization of the soil was made following the procedure recommended in Norma E196 LNEC (1966). The soil was air dried and quarted to achieve a representative sample. After quarting and removal of the organic matter visible at naked eye, the soil was passed by the 0.063 mm in a washing process. The below 0.063 mm fraction (plus water) was collected in a cup and left to settle. After settle, this fraction was left to dry and was latter weighted. The above 0.063 mm fraction was dried at 40ºC to be, after drying, passed by another sieving process. The sample was inserted in the sieves tower composed of thirteen sieves with decreasing diameter of holes (4, 2.8, 2, 1.4, 1, 0.71, 0.5, 0.355, 0.25, 0.18, 0.125, 0.09, 0.063 mm) from the top of the tower down to a catchment pan. This tower is installed in a vibrating plate. The sample was sieved for a period of 30 minutes. After that, the fraction retained in each sieve was collected and weighted.

The granulometric analysis of the fine fraction (<0.063 mm) of the soil was carried out with the use of laser diffraction instrument that consists of an optical unit, which collects the information from the scattered light when a laser is passed through the sample, determining the size of the particles in the sample. The procedure consists of dispersing the fine fraction in water that will pass by the system.

Organic matter (OM) percentage was determined by incineration of this fraction in the ceramic oven at 600ºC. By comparing the weight of sample before and after incineration, this percentage was calculated.

Carbonates percentage followed a similar method, as the sample was mixed with a strong acid (HCl) to destroy the carbonated fraction of the soil. After soil-acid mixture the sample was left to settle and the pH in the soil solution was measured (Figure 11). Deionized water was added to the soil solution until the acid neutralization. When neutralization was achieved the samples were dried and weighted. The comparison of the soil weigh before and after this process allowed for the determination of carbonates percentage.


**Figure 11 – pH determination previous to soil neutralization procedure**

Soil clay minerals composition was also determined in LNEC laboratories by difractogram. This process follows the Norma E403 LNEC (1993), where two difractograms are carried out in the fine fraction (<0.063 mm) of soil sample, one to verify the presence of expanding clays (montmorillonite) and the other in a fraction heated up to 550ºC degrees for 30 minutes for kaolinite identification.

Cation Exchange Capacity (CEC) was also determined in an external laboratory. This intrinsic property of the soil material describes the total number of exchangeable cation charges (Hillel, 1998). It's usually expressed in miliequivalents of cations per 100 grams of soil and depends not only on clay content but also on clay type. The cation exchange phenomenon affects the movement and retention of ions in the soil as well as flocculation-dispersion processes of soil colloids. pH together with CEC are very important for prediction of soil sorption capacity (Barbosa, 1999).

Porosity was determined by two similar procedures: in a simple process by saturating dry soil samples (cf. Figure 12) and from the saturated volume during soil-column experiments. The first process consisted in weighting three dry soil samples (and cups), adding water to the sample top and weight again. This simply allowed of the determination of the volume that was retained in pores, which corresponds to the porosity.

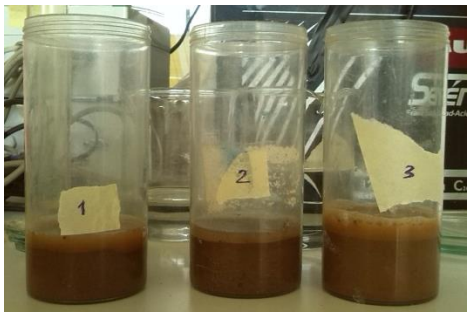



**Figure 12 – Simple experiment for density determination**

Soil porosity was also determined in these experiments using the following equation:

$$\boldsymbol{n} = \boldsymbol{V_w / V_t \, x \, 100} \, (\%)$$

where $V_w$ is the volume of water in the soil sample ($cm^3$)

$V_t$ is the total volume of the sample ($cm^3$)

Soil bulk density ($\rho_b$) ($g/cm^3$) was determined by the following equation:

$$\boldsymbol{\rho_b = W_d/V_t}$$

where $W_d$ is the weight of the dried soil sample (g).

## 4.2. Soil-column experiments methodologies and methods

A soil-column is characterized as a discrete block of soil inserted in a column that is located either outdoors or in a laboratory, allowing the control and measurement of the infiltration, as well as incorporating equipment for the total recovery of the effluent. This is usually achieved by encasing the soil column in a rigid and impermeable shell material, both for structural reasons and to prevent fluid loss (Lewis and Sjöstrom, 2010).

A set of soil-column experiments were conducted using both natural soil and soil mixture. The following sections describe the methodologies and results achieved.

### 4.2.1. Apparatus description

The soil-column experimental apparatus consists of an acrylic transparent column with 30 cm height and 5 cm diameter (Figure 13) and/or an acrylic column with 50 cm height with a similar diameter, which allowed the existence of a controlled height of water on the top of the soil, simulating the conditions of real scale infiltration basins. 30 cm column was only used in initial soil-column experiments. Following DEMEAU (2015), this material is rigid to ensure structural strength, inert to avoid chemical interference (this is particularly important when analysing emergent contaminants), transparent to facilitate visual observations of events, impermeable, and resistant to corrosion.

The soil-column is attached to a compaction system composed of a standardized weight disk for soil compaction and a ruler for dropping height determination. All columns have a tight lid base with an outlet port which is connected to a sample tube where the outflow water is collected. An inert Teflon membrane filter is added to the soil-column bottom for fine particles retention.

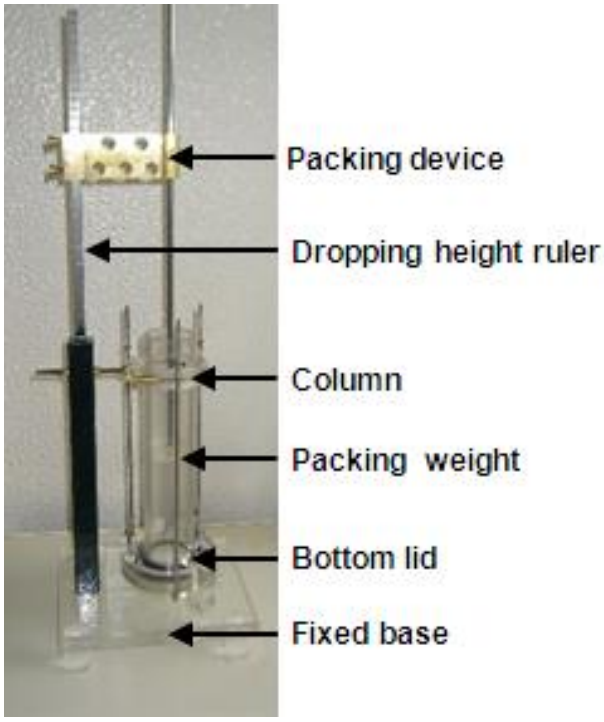



**Figure 13 – Soil-column experimental apparatus designed and built at LNEC**

For continuous water injection, a volumetric peristaltic pump was used. This peristaltic pump has a pulse volume of 3 mL and time between pulses can be adjusted. Minimum time (1s) results in a non-stop pulse making injection continuous. For pulse injection, the water was directly poured from a container to the column (Figure 14).

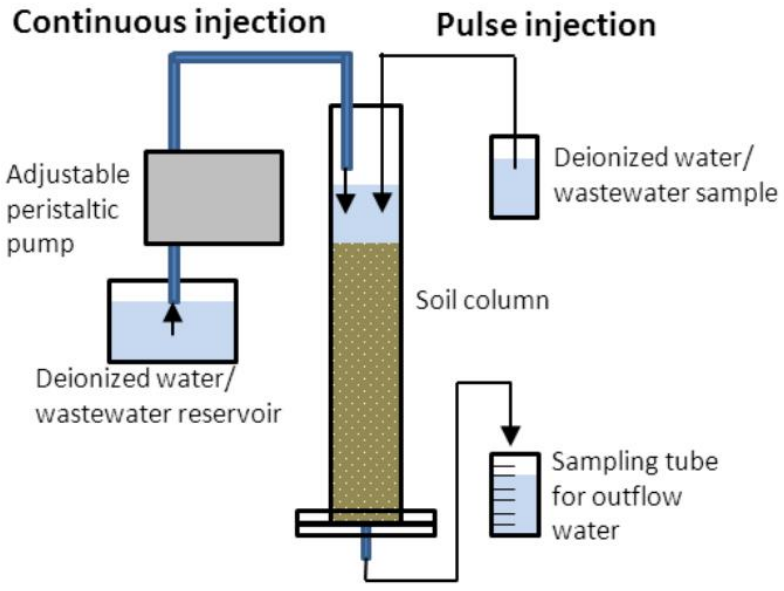



**Figure 14 – Soil-column apparatus and diagram of operation**

The injection from the wastewater/deionized water reservoir to the pump and from the pump to the column was made by PE tubes. When in contact with wastewater the tube was not used in any other experiments to avoid sample contamination. This is very important considering that pharmaceuticals occur in very small concentrations (nanograms per litre). The use of silicone tubes was discarded to avoid compound loss by reaction to tubing sections.

Outflow samples were collected at defined periods in glass graded tubes. These samples can be conditioned in dark glass vials or bottles and keep in the fridge (<4ºC) for future analysis or ultimately destroyed (if the purpose is to only characterize hydraulic behaviour of the soil). Water naturally flows from the bottom outlet to the sample tubes.

### 4.2.2. Soil and wastewater sampling procedure and experiment preparation

#### *4.2.2.1. Soil-column preparation*

Soil samples were collected at the approximate location of the infiltration site in the outskirts of SB Messines wastewater treatment plant, removing the most superficial layer, and collecting soil from a depth of 5 to 20 cm. The soil was dried at 40°C, the large organic matter (roots, leaves, etc.) was manually removed; afterwards it was quartered and split in equal portions to be representative of the site soil.

The soil-column experiments were performed in a soil subject to a dry pack procedure. The objective of packing is to produce a homogeneous soil column having a bulk density similar to that observed naturally, while avoiding the formation of preferential flow pathways. This might be the most critical issue associated with soil-column experiments (Lewis and Sjöstrom, 2010), since these preferential flow paths will result in spatial heterogeneity in flux and solutes transport, and will significantly bias any experimental results.

Dry or damp packing involves loading small discrete amounts or “lifts” of dry or damp soil into the column and then mechanically packing it either by hand or with some type of ram or pestle (Lewis and Sjöstrom, 2010). After the column assembling and the Teflon filter correctly positioned at the bottom end section, the soil-column was filled with the soil following the CEN/Technical Specification 14405 (2004): fill the column in 5 cm soil sections packing each section with the weight, dropping it three times over a 20 cm height above it. In this process the whole surface should be covered with the weight disk after three drops for maximum regularization. The surface was then scarified before addition of another 5 cm layer. The process was repeated until the column was completely filled. The soil-column was then weighted. This compaction method was applied to all soil-columns except Column 5, where the number of weight drops was reduced to two instead of three.

As stated above, the removal of roots, leaves and big sized organic will help, after compaction, to decrease the probability of macropore flow to occur. This phenomenon refers to any preferential flow due to heterogeneities within the porous medium, including cracks, root holes, wormholes and macropores.

#### *4.2.2.2. Wastewater sampling*

Wastewater effluent samples were collected in the SBM WWTP point of discharge. In-situ parameters were measured and samples for analysis were collected in 1L dark glass bottles for pharmaceuticals and 40 mL dark glass vials for other parameters analysis. For injection in soil-column experiments, different campaigns for collecting the necessary water were conducted. This water was collected and transported to LASUB in a large 25L container, where it was fractioned in several smaller glass containers.

As stated before, both samples collected from SBM WWTP effluent and from the columns bottom outlet are stored in chilled environment to prevent alteration (<4°C) until analysis. ECs are potentially sensitive to UV radiation, so dark glass bottles were used to prevent photo degradation, particularly for pharmaceuticals analysis (DEMEAU, 2015).

The outflow samples were collected once the volume necessary for analysis was achieved, except for pharmaceuticals. Due to the large volume necessary (which corresponded to several pore-volumes to every column) and the time needed to achieve it, the samples collected for pharmaceuticals where kept in totalizer bottles. This means that the pharmaceuticals samples were related to an extended period of time, being this the main reason for the smaller number of samples for pharmaceuticals compared to the other parameters. The totalizer bottles were also kept in refrigerated conditions.

#### *4.2.2.3. Natural soil used*

To correctly define the soil parameters and to recreate/model different functioning conditions, several soil-column experiments were conducted using the same natural soil subject to altered methods of packing, water matrix, soil thickness and granulometry, time of experiment, injection and saturation conditions. Table 8 presents a synthesis of the operating details of the soil-column experiments conducted in the natural soil. Uncertainty factors are also taken into account and are briefly discussed in Section 6.1.

**Table 8 - Synthesis of the operating details of the soil-column experiments conducted in the natural soil**

| | **Column 1** | **Column 2** | **Column 3** | **Column 4** | **Column 5** |
|---|---|---|---|---|---|
| Column height (cm) | 30 | 30 | 30 | 50 | 50 |
| Soil thickness (cm) | 30 | 30 | 20 | 30 | 30 |
| Sieved (> 2 mm) | No | Yes | Yes | Yes | Yes |
| Soil packing | Specific weight - 3 strikes | Specific weight - 3 strikes | Specific weight - 3 strikes | Specific weight - 3 strikes | Specific weight - 2 strikes |

| | Column 1 | Column 2 | Column 3 | Column 4 | Column 5 |
|---|---|---|---|---|---|
| Saturation conditions | Started saturated Always saturated | Started saturated Always saturated | Started saturated Always saturated | Started saturated Unsaturated/ saturated cycles | Started saturated Unsaturated/ saturated cycles |
| Injection method | Continuous | Continuous | Continuous | Continuous/ pulse | Pulse |
| Inert sand layer on soil top | No | No | No | Yes (0.5 cm) | Yes (0.5 cm) |
| Water matrix | Deionized | Deionized | Deionized/ Wastewater | Wastewater | Deionized/ Wastewater |
| Experiment time length (days) | 1 | 0.2 | 5 | 33 | 16 |
| Outflow chemical analysis | No | No | Yes | Yes | Yes |

In total, five soil-column experiments were conducted using natural soil, named Column 1 to Column 5. In all experiments the soil used had the same volume, corresponding to 30 cm height and 5 cm diameter, except for Column 3 where the height was 20 cm.

For Column 2 to 4 the soil, which has the tendency to form clay aggregates, was disaggregated in a mortar and then sieved, having the particles larger than 2 mm being excluded from the column filling sample – as stated in Section 4.3.1.1, 84.1% of SBM soil particles are below 2 mm size. Accordingly to Hillel (1998), large rocks in soil do not behave like soil, and if numerous large rocks occur this might affect the behaviour of soil. For such high composition in sand in SBM soil, being the most representative fraction, it's advisable to take larger fractions (gravel). This also allowed for the reduction of possible air pockets (that could result in preferential flow paths) with better particle rearrangement inside the column.

**Figure 15 – Clay aggregates in natural soil at SB Messines**

In the top section of Columns 4 and 5 a non-reactive permeable layer was used to ensure an equal distribution of the input water and minimum disturbance of the first layer of soil during the water injection, also preventing an early clogging process. This layer was composed of Fontainebleu quartz white sand with an approximate thickness of 0.5 cm.

For all five soil-column experiments the soil was completely saturated with deionized water from bottom to top for about 16 hours allowing the reduction of air-pockets inside the soil – Figure 16. This saturation process can mainly prevent fingering phenomena, which refers to the preferential flow taking place as a result of the wetting front instability, and by a number of reasons, includes changes in hydraulic conductivity with depth and compression of air ahead of the wetting front. Fingering is most likely to occur in soils that are predominantly sandy and that are initially extremely dry (DEMEAU, 2015).

**Figure 16 – Saturation process from the column bottom (Column 1)**

Concerning the injection method for the experiment, after saturation, all columns except Column 5 have started with continuous flow from the top using an automatic peristaltic pump. Column 4 experiments started with continuous flow until the end of the first day, and the injection method was switched to pulse injection. Column 5 started with pulse injection of approximately 378 mL of deionized water, filling the 20 cm top of the column,

Column 1 and 2 have used deionized water for all experiment time length while the other columns added SBM WWTP effluent water injected. Column 3 experiment, started with continuous deionized water injection and it was switched to wastewater after 30 minutes. In column 4 only wastewater was used, while column 5 add 2 cycles of deionized water between 2 wastewater injection cycles.

Following DEMEAU (2015), the transparent parts of the setup were wrapped in aluminium foil to simulate non-light conditions encountered in the subsurface, and to reduce photolithotrophic microorganisms growth of and photodegradation of contaminants - Figure 17.

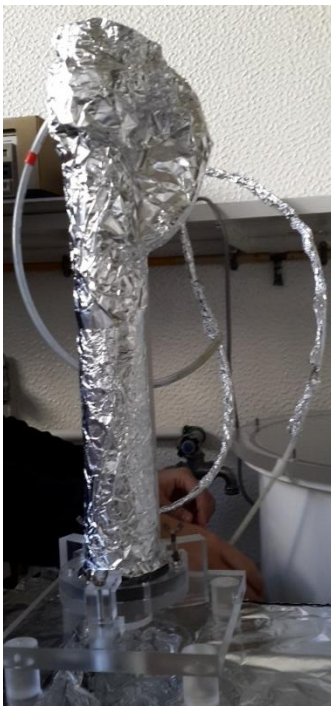


**Figure 17 – Transparent parts of the column covered with tinfoil paper**

The experiments were held in different time periods, from a few hours (Column 2) to several days (Column 3, 4 and 5). For Columns 4 and 5 an unsaturation period was considered after every injection period in order to recreate the field conditions for contaminant degradation enhancement through oxygenation process. The different experiments aimed to assess the importance that compaction procedures, saturation-desaturation and infiltration water quality can have in the flow rate of the same soil, also for different time periods.

#### *4.2.2.4. Soil mixture used*

Considering the interesting results of project ENSAT (Section 2.5) that used a reactive layer installed in the bottom of the SAT-MAR infiltration basin, as well as the results obtained from the soil-column experiments using the natural soil, it was decided that a similar approach could be taken into account in Portugal MARSOL DEMO site of Querença-Silves. Following Section 1.3 objectives, a reactive layer was created by the mixture of different materials. The quality of the outflow water and hydraulic behaviour of both the natural soil and the soil mixture were compared and will be taken into account in the selection of the best material to be used in the infiltration basins.

Concerning the materials to be used, several options were considered. The main factors for the selection were essentially that those materials were cheap and easily available (if possible, wastes resulting from agricultural, recycling or industrial processes), that do not represent risks for the environment, and that can be easily handled during the construction process. It was taken into account that the materials should be collected near or from the area of the installation, which would greatly reduce the transportation cost.

After a brief literature review and a set of personal contacts, the list of possible materials was widened. Several initially considered were later excluded for several factors. An example of these materials is cork, carob ("alfarroba") and almond external bark. Cork showed itself a not so good material for contaminant retention given its hydrophobic and impermeable behaviour, as presented by Pintor *et al.* (2012). Also due to its density cork particles tend to fluctuate making it very hard to install in the bottom of infiltration basins. Finally, this material is not cheap.

Carob is easily available on Algarve. Unfortunately the carob external skin also shown signs of hydrophobic behaviour as well as it tend to rapidly rot and moulder when in continuous contact with water, which would greatly decrease the lifespan of the reactive layer. Also due to its constitution benefits to human health, carob has seen a price increase, being increasingly used in flour/food production besides other industrial and agricultural uses.

Almond external bark, which may have been a good material for mixture with the soil, was not tested since it did not comply with the factors stated above: this material is neither cheap nor easily available in the study area, mainly because, due to its calorific power it is commonly used in industrial ovens or households heating systems. Secondly, although almond trees are very common in Algarve, the business of almond has seen a decrease in value due to the more accessible prices in emergent markets. Because of this, almond trees are being replaced by orange trees and other more valuable cultures in the last years.

Other options had to be taken into account. Following ENSAT (2012) method and considering that upper soil layers with the higher organic matter content have the potential to accumulate some pharmaceuticals such as carbamazepine during flooding/drainage cycles (Arye *et al.*, 2011), an organic soil was selected. A commercial organic soil was acquired for the experiments. Special attention was taken to its composition as the most common use of commercial organic soil is plants fertilization. The acquired organic soil has an organic matter percentage above 70% and it's composed by 70% humus resulting from natural composting and 25% peat. The remaining percentage is fine sand. Given that peat tends to present high porosities (Walczak *et al.*, 2002) better performance is to be expected in soil oxygenation.

In fact, a large percentage of organic matter can greatly contribute to the increase of biological activity and therefore the chances of biodegradation processes to occur as it has a supply of dissolved organic carbon.

Another factor that had to be taken into account was the hydraulic behaviour – although time of contact is essential for contaminant retention, it is also important that this reactive layer does not behave as a cap layer. This would result in very long periods of ponding which would possibly create other problems in the area of infiltration.

To increase the soil mixture permeability an "artificial sand" was selected. Basically, this component results from the industrial extraction of inert materials for construction, more specifically limestone, common in Algarve. This "artificial sand" results from the crushing of limestone into specified particle sizes for different uses. It's easily available in the study area. The selected particle size, available to sell, was 0-2 mm.

In a soil mixture this material will help to increase the sand fraction and also the porosity, allowing for infiltration and also for the reactive layer to "breathe" in the unsaturated periods.

The fact that this artificial sand is composed of crushed limestone can have another benefit, mainly in the quality improvement aspect. Crushing allowed for a larger reactive surface to be available in each grain which facilitates surface retention and cationic exchange processes. Also, as limestone can present large concentrations of calcium (Ca) and magnesium (Mg), cationic exchange and retention processes can be enhanced by the substitution in rock matrix of Ca and Mg. Ca and Mg displacement as a result of cation exchange processes can result in fixation of other elements such as heavy metals (Barbosa, 1999).


**Figure 18 – Different soil mixture components (artificial sand – left cup; natural soil (disaggregated and sieved) – middle cup; organic soil – right cup)**

The mixing process was relatively simple: taking into account the material percentage to be considered in each mixture, each fraction was weighted in the defined proportions and added. This bulk compound was then hand mixed for the sample to be the most homogeneous as possible. The mixture was then packed into the column following the procedure explained at Section 4.2.2.3.

The choice of having a soil mixture of different materials instead of having layers of each selected material inserted into the column, aims to decrease uncertainty factors related to water flow inside the column: the creation of different layers inside can create hydraulic barriers with different behaviour that can hinder the water flow, and create preferential ways or even ponding or retention in certain parts of the column. The homogeneous soil mixture along the column avoids changes in flow behaviour from top to bottom, making it as regular as possible, which is easier to reproduce and numerically model. The soil mixture as a whole can insure that the behaviour along the column concerning quality factors is also the same. It is also very difficult to reproduce this layering process at the basin scale.

To firstly understand the hydraulic behaviour of the soil mixture, several soil-column experiments with different materials percentages in composition were conducted, as demonstrated in Figure 19 – Column 6 to Column 7.

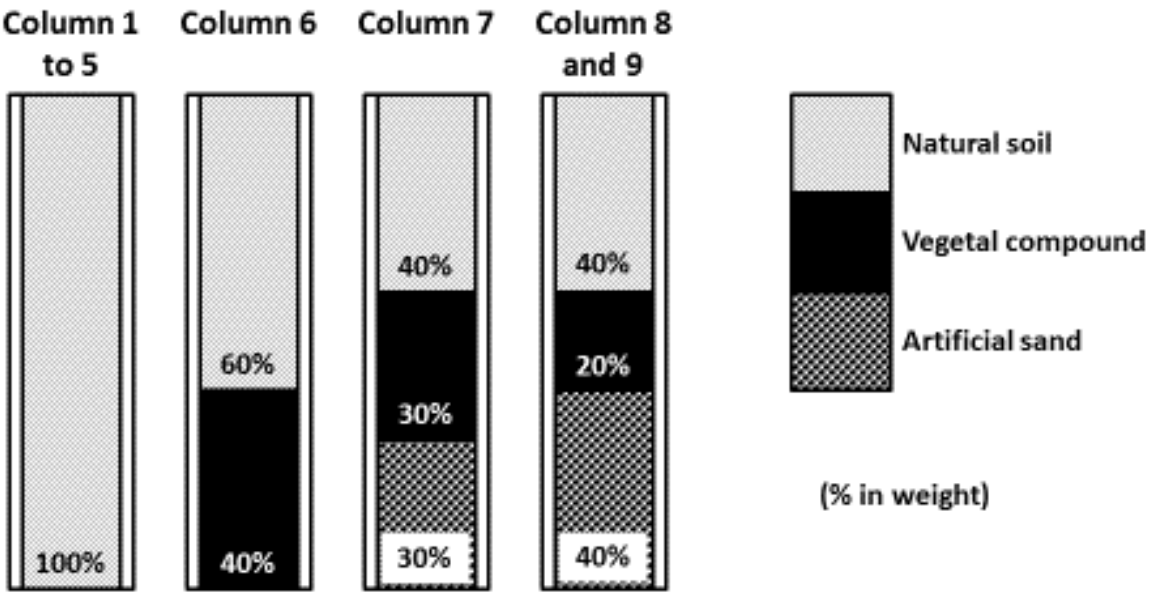



**Figure 19 – Soil composition in conducted soil-column experiments**

Column 6 had a composition of 60% of natural soil and 40% of organic soil while Column 7 had 40% of natural soil, 30% of organic soil and 30% of artificial sand. These two soil-column experiments were conducted at the same time, and allowed to understand the effect of artificial sand presence in the hydraulic behaviour.

In Column 8 and Column 9, both with same soil mixture composition, a smaller percentage in weight of vegetal compound was used. The causes for the change in composition are discussed in Section 4.3.2.2.

Quality parameters where only measured in these two last columns, after measuring that a good hydraulic behaviour has been achieved. The purpose of this remains with the fact that large quantities of volume is needed for pharmaceuticals analysis (approximately 1 L) – having two columns with same soil composition working in parallel, assembled with equal packing and injection methods, volumes and water matrix, can be understood as being the same column. So, Column 9 outflow water was collected exclusively for pharmaceuticals analysis while Column 8 outflow water was used to analyse all the other parameters.

The details concerning the four soil-column experiments conducted in different soil mixtures are summarized in Table 9.

**Table 9 - Synthesis of the operating details of the soil-column experiments conducted in the soil mixture**

| | Column 6 | Column 7 | Column 8 | Column 9 |
|---|---|---|---|---|
| Column height (cm) | 50 | 50 | 50 | 50 |
| Soil thickness (cm) | 30 | 30 | 30 | 30 |
| Sieved (> 2 mm) | Yes | Yes | Yes | Yes |
| Soil packing | Specific weight - 3 strikes | Specific weight - 3 strikes | Specific weight - 3 strikes | Specific weight - 3 strikes |
| Saturation conditions | Started saturated Always saturated | Started saturated Always saturated | Started saturated Unsaturated/saturated cycles | Started saturated Unsaturated/saturated cycles |
| Injection method | Continuous | Continuous | Pulse | Pulse |
| Inert sand layer on soil top | Yes (0,5 cm) | Yes (0,5 cm) | Yes (0,5 cm) | Yes (0,5 cm) |
| Water matrix | Deionized water | Deionized water | Wastewater | Wastewater |
| Experiment time length (days) | 4 | 4 | 46 | 46 |
| Outflow chemical analisys | No | No | Yes | Yes |

### 4.2.3. Parameters selected for quality analysis

Considering that wastewater matrix can be very different for each WWTP (given certain factors such number of population served, age of population, seasonal effects, etc.) the parameters to be analysed in the soil-column inflow and outflow had to be handpicked specifically.

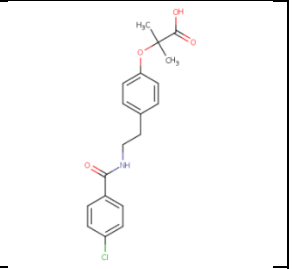
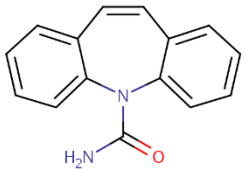
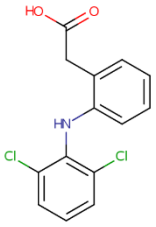
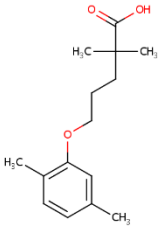
In-situ parameters such as pH, Eh, temperature and electrical conductivity were measured in wastewater prior to each injection pulse (Column 4 to Column 5) and during the experiments in each sample collected in the column outflow.

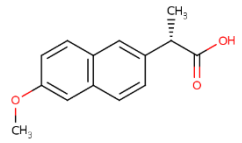
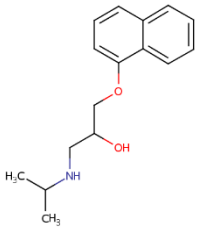
Considering the parameters for chemical analysis, three “tracers” that commonly occur in wastewater where selected due it its stability in aqueous media – boron, copper and zinc, and to their presence in the groundwater downgradient the SBM WWTP rejection point (Leitão *et al.*, 2014).

Another component which is fundamental, not only to characterize the wastewater matrix but also to understand the processes that occur inside the column and the success of soil as filtering layer is nitrogen. Nitrogen cycle offers good information about the conditions inside the column. Therefore, nitrates, nitrites and ammonia were determined. Also, phosphorous is an important component in this type of water, so phosphates were considered in the analysis. Complementary information was also collected on sulphates.

Concerning the pharmaceuticals, and given the knowledge achieved in Section 2.5, special attention was given to those that are prevalent in wastewater effluent, such as bezafibrate, carbamazepine, diclofenac, gemfibrozil, naproxen and propranolol. The characteristics of these compounds are presented in Table 10. All pharmaceuticals examined are presented in the following results sections (4.3.1.3).

**Table 10 – Summary of most relevant analysed pharmaceuticals (adapted from www.drugbank.ca)**

| Pharmaceutical | Therapeutic use | Structure |
|---|---|---|
| Bezafibrate | Antilipemic agent that lowers cholesterol and triglycerides. It decreases low density lipoproteins (LDL) and increases high density lipoproteins (HDL). |  |
| Carbamazepine | An anticonvulsant used to control grand mal and psychomotor or focal seizures. Its mode of action is not fully understood. |  |
| Diclofenac | A non-steroidal anti-inflammatory agent (NSAID) with antipyretic and analgesic actions. |  |
| Gemfibrozil | A lipid-regulating agent that lowers elevated serum lipids primarily by decreasing serum triglycerides with a variable reduction in total cholesterol. |  |

| Pharmaceutical | Therapeutic use | Structure |
|---|---|---|
| Naproxen | Anti-inflammatory agent with analgesic and antipyretic properties. Used in the treatment of rheumatoid arthritis and other rheumatic or musculoskeletal disorders, dysmenorrhea, and acute gout. |  |
| Propanolol | Used in the treatment or prevention of many disorders including acute myocardial infarction, arrhythmias, angina pectoris, hypertension, hypertensive emergencies, hyperthyroidism, migraine, menopause, and anxiety. |  |

After Column 3 experiment was finished, and as it was a “learn as we go” process, it was decided to expand the number of parameters to be analysed. This way the maximum quantity information would be collected, and processes inside the column could be understood. So, in addition with other previously described measured parameters, the following set was considered – Table 11.

**Table 11 – List of new analysed parameters**

| Parameter | | | |
|---|---|---|---|
| Aluminium | Calcium | Lithium | Potassium |
| Antimony | Chloride | Magnesium | Selenium |
| Arsenic | Chromium | Manganese | Silver |
| Barium | Cobalt | Molybdenum | Sodium |
| Beryllium | Iron | Nickel | Thallium |
| Cadmium | Lead | Phosphorus | Vanadium |

The results from the inflow wastewater (WW) analysis for the soil-column experiments are presented in Table 12. Pharmaceuticals concentrations are presented in Table 13.

**Table 12 – Inflow WW (SBM WWTP effluent) analysis results**

| | | Column 3 | Column 4 & Column 5 | Column 8 & Column 9 |
|---|---|---|---|---|
| **Sampling date** | | 17-11-2014 | 17-02-2015 | 20-05-2015 |
| **Temperature** | **ºC** | 15.7 | 11.7 | 19 |
| **pH** | | 6.08 | 7.61 | 7.28 |
| **Eh (mV)** | | - | 173 | 90 |
| **Conductivity** | **µS/cm** | 760 | 649 | 888 |
| **Boron** | **mg/L** | 0.236 | 0.235 | 0.723 |
| **Copper** | **mg/L** | 0.0055 | <0.002 | 0.0033 |
| **Zinc** | **mg/L** | 0.035 | 0.0027 | 0.0049 |

| | | Column 3 | Column 4 & Column 5 | Column 8 & Column 9 |
|---|---|---|---|---|
| **Ammonia** | **mg/L** | 32.8 | 34.2 | 48.9 |
| **Nitrates** | **mg/L** | <2 | <2 | <2 |
| **Nitrites** | **mg/L** | 0.0176 | <0.005 | 0.0104 |
| **Phosphate** | **mg/L** | 6.32 | 7.68 | 15.2 |
| **Sulphate** | **mg/L** | 88 | 64.7 | 70.9 |
| **Aluminium** | **mg/L** | 0.014 | 0.011 | 0.057 |
| **Antimony** | **mg/L** | <0.01 | <0.01 | 0.083 |
| **Arsenic** | **mg/L** | <0.005 | <0.005 | <0.005 |
| **Barium** | **mg/L** | 0.0673 | 0.0523 | 0.18 |
| **Beryllium** | **mg/L** | <0.0002 | <0.0002 | <0.0002 |
| **Cadmium** | **mg/L** | <0.0004 | <0.0004 | <0.0004 |
| **Calcium** | **mg/L** | 29.4 | 43.6 | 37.8 |
| **Chromium** | **mg/L** | 0.0011 | <0.001 | 0.0022 |
| **Cobalt** | **mg/L** | <0.002 | <0.002 | <0.002 |
| **Iron** | **mg/L** | 0.0362 | 0.0408 | 0.0634 |
| **Lead** | **mg/L** | <0.005 | <0.005 | <0.005 |
| **Lithium** | **mg/L** | <0.001 | 0.0012 | 0.0167 |
| **Magnesium** | **mg/L** | 17.4 | 29 | 28.4 |
| **Manganese** | **mg/L** | 0.0627 | 0.0387 | 0.0572 |
| **Molybdenum** | **mg/L** | <0.002 | <0.002 | 0.0024 |
| **Nickel** | **mg/L** | <0.002 | 0.0021 | 0.0069 |
| **Phosphorus** | **mg/L** | 4.73 | 2.79 | 5.52 |
| **Potassium** | **mg/L** | 16.7 | 14.8 | 23.6 |
| **Selenium** | **mg/L** | <0.01 | <0.01 | 0.027 |
| **Silver** | **mg/L** | <0.001 | <0.001 | 0.0013 |
| **Sodium** | **mg/L** | 58 | 71.6 | 92.5 |
| **Thallium** | **mg/L** | <0.01 | <0.01 | 0.074 |
| **Vanadium** | **mg/L** | <0.001 | <0.001 | 0.0055 |
| **Chloride** | **mg/L** | NA | 91.1 | 118 |

Note: NA – not analysed

From the set of 32 parameters analysed, Column 3 had 17 values above the limit of recovery (LOR), Column 4 and Column 5 had 17 and Column 8 and Column 9 had 26. Chloride was not measured for Column 3 inflow water due to lack of sampling volume available.

**Table 13 - Inflow WW (SBM WWTP effluent) analysis results concerning pharmaceuticals**

| | | Column 3 | Column 4 & Column 5 | Column 8 & Column 9 |
|---|---|---|---|---|
| **Sampling date** | | 17-11-2014 | 17-02-2015 | 20-05-2015 |
| **Atenolol** | **µg/L** | NA | 0.27 | 0.06 |
| **Acetylsalicylic acid** | **µg/L** | NA | <0.02 | <0.02 |
| **Betaxolol** | **µg/L** | NA | 0.01 | <0.01 |
| **Bezafibrat** | **µg/L** | NA | 0.1 | <0.01 |
| **Bisoprolol** | **µg/L** | NA | 0.09 | 0.03 |

| | | Column 3 | Column 4 & Column 5 | Column 8 & Column 9 |
|---|---|---|---|---|
| **Carbamazepine** | **µg/L** | NA | 0.48 | 0.73 |
| **Clofibrin acid** | **µg/L** | NA | <0.02 | <0.02 |
| **Diazepam** | **µg/L** | NA | <0.01 | <0.01 |
| **Diclofenac** | **µg/L** | NA | 0.48 | 0.15 |
| **Etofibrat** | **µg/L** | NA | <0.02 | <0.02 |
| **Fenofibrat** | **µg/L** | NA | <0.04 | <0.04 |
| **Fenoprofen** | **µg/L** | NA | <0.02 | <0.02 |
| **Gemfibrozil** | **µg/L** | NA | 0.29 | 0.4 |
| **Ibuprofen** | **µg/L** | NA | 0.06 | <0.01 |
| **Indometacin** | **µg/L** | NA | 0.03 | <0.02 |
| **Ketoprofen** | **µg/L** | NA | <0.01 | <0.01 |
| **Metoprolol** | **µg/L** | NA | 0.07 | 0.04 |
| **Naproxen** | **µg/L** | NA | 0.56 | 0.17 |
| **Pentoxifyllin** | **µg/L** | NA | 0.24 | <0.01 |
| **Phenacetin** | **µg/L** | NA | <0.01 | <0.01 |
| **Phenazon** | **µg/L** | NA | <0.01 | <0.01 |
| **Pindolol** | **µg/L** | NA | <0.01 | <0.01 |
| **Propanolol** | **µg/L** | NA | 0.05 | 0.02 |
| **Sotalol** | **µg/L** | NA | 0.08 | 0.05 |

Note: NA – not analysed

In the pharmaceuticals results, from the 24 parameters analysed, 14 were above LOR for Column 4 and Column 5 inflow, while for Column 8 and Column 9, nine parameters were above LOR. The first set (Column 4 and Column 5) presents, in general, higher concentrations in detected compounds (above LOR) when compared to the second (Column 8 and Column 9), except for Carbamazepine and Gemfibrozil. Inflow water parameters concerning pharmaceuticals where not determined for Column 3.

This set of information will be used for column outflow concentration comparison in Section 4.3.1.3 (natural soil) and Section 4.3.2.3 (soil mixture).

## 4.3. Soil-column experiments results

In this section the main results of all the experiments conducted will be presented, for both natural soil and soil mixture.

### 4.3.1. Natural soil

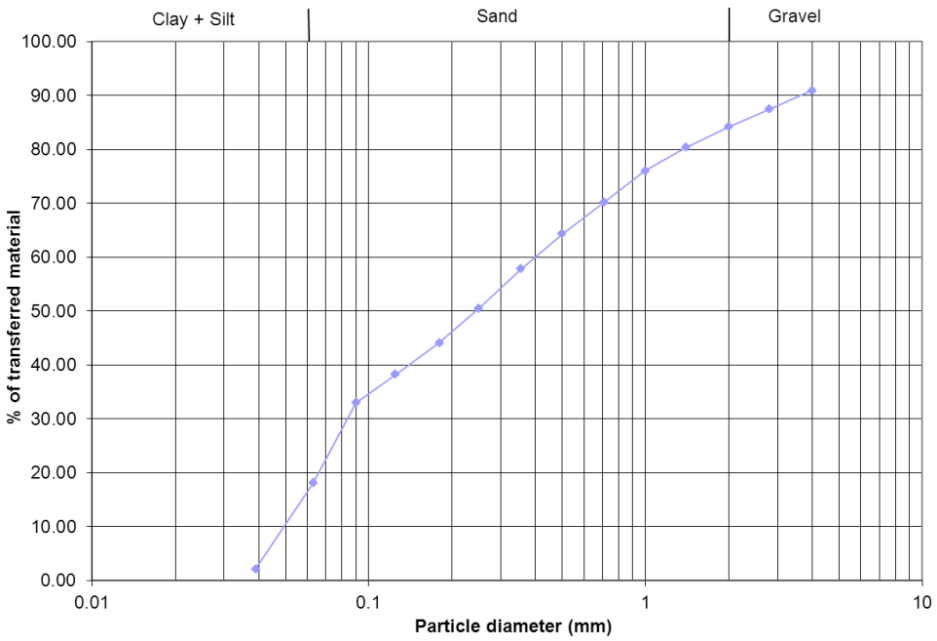
Below are presented the overall soil-column experiment and characterization data for the São Bartolomeu de Messines natural soil.

#### 4.3.1.1. Soil characteristics

In this section the results are presented accordingly to the methods that were explained in Section 4.1.

Granulometry analysis allowed to determine that SBM natural soil is mainly composed of sand (81.91%) with a small fraction of silt (15.95%) and clay (2.14%). The granulometric curve is presented in Graph 5. Representing these results in the textural triangle, this soil is classified as a Loamy Sand.

This data will be fundamental in numerical modelling (Section 5).




**Graph 5 – Granulometric curve for SBM natural soil**

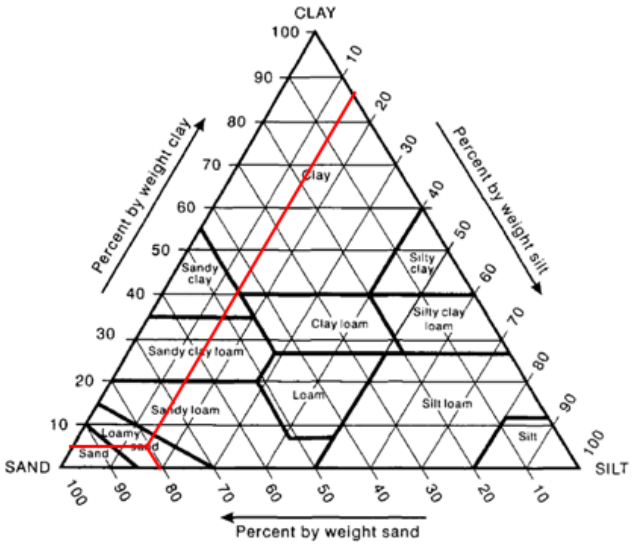



**Figure 20 – Textural triangle (adapted from Hillel, 1998)**

Cation Exchange Capacity (CEC) and soil solution pH results are presented in Table 14.

**Table 14 – Natural soil CEC and pH results ([d] – Bascomb method)**

| pH | CEC [d] (cmol/kg of soil) |
|---|---|
| 8.90 | 5.74 |

The SBM natural soil presents a typical loamy sand CEC value (between 5 and 10 cmol/kg of soil[2]) and high alkalinity. High alkalinity (or alkali) soils may result from high concentrations of $CaCO_3$ resulting from limestone weathering, which is expected in this area given that the most common lithology is limestone (see Section 3). These soils are often incipient and present low permeability[3].

Concerning mineral composition, the sample of SBM natural soil presented the following results (Figure 21):

- Minerals in greater proportion – quartz, calcite, montmorillonite (bentonite) and feldspar (anorthite).
- Minerals in trace proportion – dolomite, mica (illite), kaolinite and hematite.

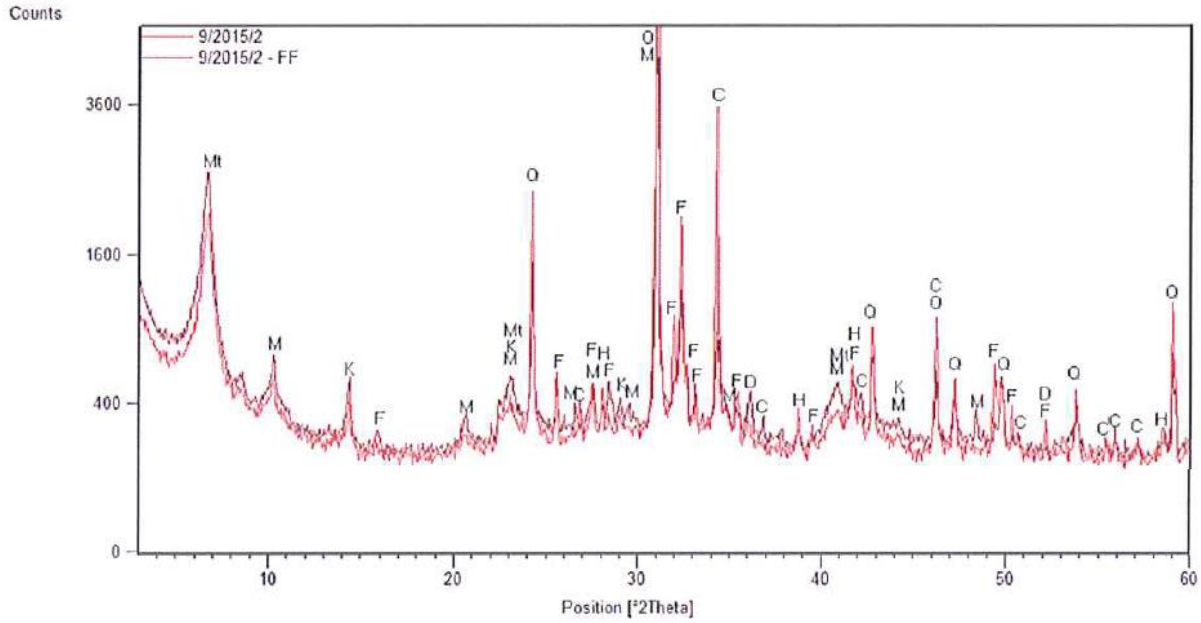



**Figure 21 – SBM soil difractogram to normal (9/2015/2) and below 0.063 mm (9/2015/2 – FF). (Mt – Montmorillonite, M – Mica, K – Kaolinite, F – Feldspar, Q – Quartz, C – Calcite, D – Dolomite, H – Hematite)**

This mineral proportion may represent a conjugation of two syntheses for this soil, as it is between Triassic sandstone and Jurassic limestones contact area, therefore having large quantities of quartz and calcite, and traces of iron oxides.

[2] https://en.wikipedia.org/wiki/Cation-exchange_capacity; http://extension.uga.edu/publications/detail.cfm?number=C1040
[3] https://en.wikipedia.org/wiki/Alkali_soil

The relatively large percentage of carbonates determined in soil composition (24.02%) is coherent with the information above. It also presents a low organic matter percentage (2.66%), which was expected given the low CEC value.

Bulk density and porosity, determined by the two methods presented in Section 4.1, are presented in Table 15 and Table 16. Table 15 also presents humidity percentage in soil.

**Table 15 – Porosity and bulk density results**

| | Sample 1 | Sample 2 | Sample 3 |
|---|---|---|---|
| **Humidity (%)** | 17.98 | 17.26 | 16.20 |
| **Porosity (%)** | 41.29 | 39.24 | 38.50 |
| **Bulk density ($g/cm^3$)** | 1.09 | 1.12 | 1.13 |

**Table 16 – Porosity and bulk density from soil-column experiments**

| | Column 1 | Column 2 | Column 3 | Column 4 | Column 5 |
|---|---|---|---|---|---|
| **Porosity (%)** | 45.9 | 43.1 | 44.1 | 43.4 | 41.8 |
| **Bulk density ($g/cm^3$)** | 1.39 | 1.38 | 1.44 | 1.52 | 1.46 |

SBM soil presents a slightly high percentage of retained water in its composition (17.15%). This may be related with silt/clay fraction.

Concerning porosity, the soil presents a relatively large porosity percentage, typical of sands[4]. Obtained values are similar in both methods, but slightly higher in soil-column experiments (average – 43.6%) (average of simple method – 39.7%).

Average bulk density determined from simple method is 1.11 $g/cm^3$ while slightly higher values are again observed in the soil-column experiments (average of 1.44 $g/cm^3$). This difference may be associated with packing method that is applied only to soil-column experiments. In simple method the soil samples were only poured to the container without any packing method, therefore the lower bulk density. Besides these disparities between methods, these values are acceptable for fine loamy sand (Domenico and Schwartz, 1998; Lewis and Sjöstrom, 2010) – Table 17.

**Table 17 – Average range of bulk densities and porosities of typical unconsolidated soils (adapted from Domenico and Schwartz, 1998)**

| Type of soils | Porosity range (%) | Bulk density range ($g/cm^3$) |
|---|---|---|
| **Coarse gravel** | 24 - 36 | 2.0 - 1 .7 |
| **Fine gravel** | 25 - 38 | 2.0 - 1.6 |
| **Coarse sand** | 31 - 46 | 1.8 - 1.4 |
| **Fine Sand** | 26 - 53 | 2.0 - 1.2 |
| **Silt** | 34 - 61 | 1.7 - 1.0 |
| **Clay** | 34 - 60 | 1.7 - 1.0 |

[4] http://web.ead.anl.gov/resrad/datacoll/porosity.htm

#### *4.3.1.2. Soil hydraulic behaviour*

Soil hydraulic behaviour was analysed taking into account the column outlet flow rates, and consequently permeability, for all soil-column experiments conducted using SBM natural soil. The main results are summarized in Table 18. Flow rate and permeability results are presented as average for two periods of time – average obtained at first day of experiment (Day 1 line) and average obtained for all the experiment time length (Experiment time line).

**Table 18 – Natural soil-column experiments results for flow**

| | | Column 1 | Column 2 | Column 3 | Column 4 | Column 5 |
|---|---|---|---|---|---|---|
| **Pore-volume (mL)** | | 270.1 | 253.5 | 173.2 | 266.1 | 256.3 |
| **Experiment time length (days)** | | 1 | 0.11 | 4.26 | 32.99 | 15.92 |
| **Flow rate ($cm^3$/min)** | **Day 1** | 0.846 | - | 0.869 | 0.363 | 1.504 |
| | **Experiment time** | 0.846 | 1.457 | 0.789 | 0.174 | 0.543 |
| **Permeability (m/d)** | **Day 1** | 1.353 | - | 1.445 | 0.589 | 2.536 |
| | **Experiment time** | 1.353 | 2.480 | 1.312 | 0.282 | 0.915 |

Concerning the calculated pore-volume for each column, similar values were obtained for each column (considering that the pore-volume for column 3, with 20 cm, is 173.2 mL × 3/2 is 259.8 mL) – for a 30 cm soil layer in a 5 cm diameter column an average pore-volume of 261.16 mL. The slightly above average pore-volume obtained for Column 1 experiment may result from the fact that the soil was not sieved nor disaggregated, which created a large number of cavities due to the large granulometric heterogeneity (Figure 22).

**Figure 22 – Detail of Column 1 (unsaturated)**

As previously stated, column experiments were conducted through different time periods, from several hours (Column 2) to 1 month (Column 4). This allowed the observation of the flow rate variation though time in different levels of detail.

Having as reference the column behaviour for 1 day, it's possible to observe several variations throughout the five columns (Table 18). Column 4 presents the worst result at the end of this period in terms of flow rate (0.363 $cm^3$/min) and permeability (0.589 m/d). On the other hand, Column 5 presented the best results, with a flow rate and permeability four times larger than

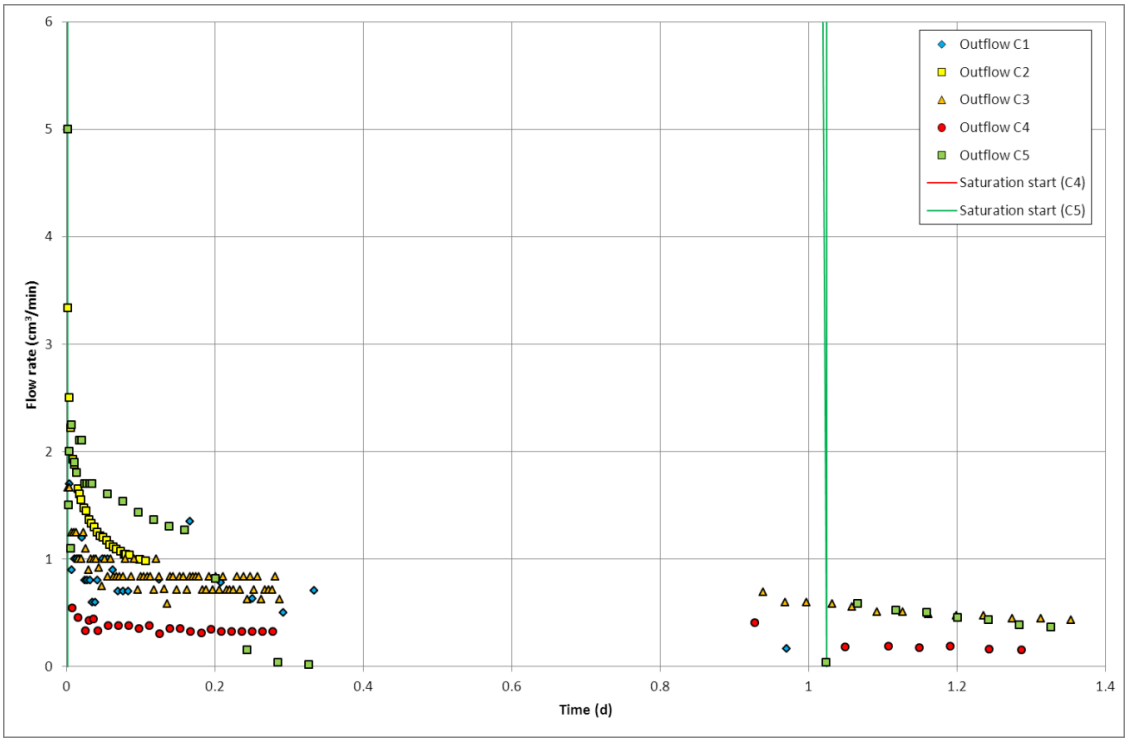
in Column 4. It can be assumed that these discrepancies are a direct result from the assembling and packing methods as described in Section 4.2.1, Table 8, given that Column 5 packing only took 2 strikes instead of 3 in Column 4 and the first cycles used deionized water (= lower biological and organic content therefore lower possibility for clogging) instead of wastewater.

If a linear behaviour is considered by observing this parameters for all the time of the experiment is possible to see that it tends to decrease through time – Flow rate of experiment at C1 (0.846 $cm^3$/min), C2 (1.457 $cm^3$/min) and C3 (0.789 $cm^3$/min) where the longest is C3 and the shortest is C2.

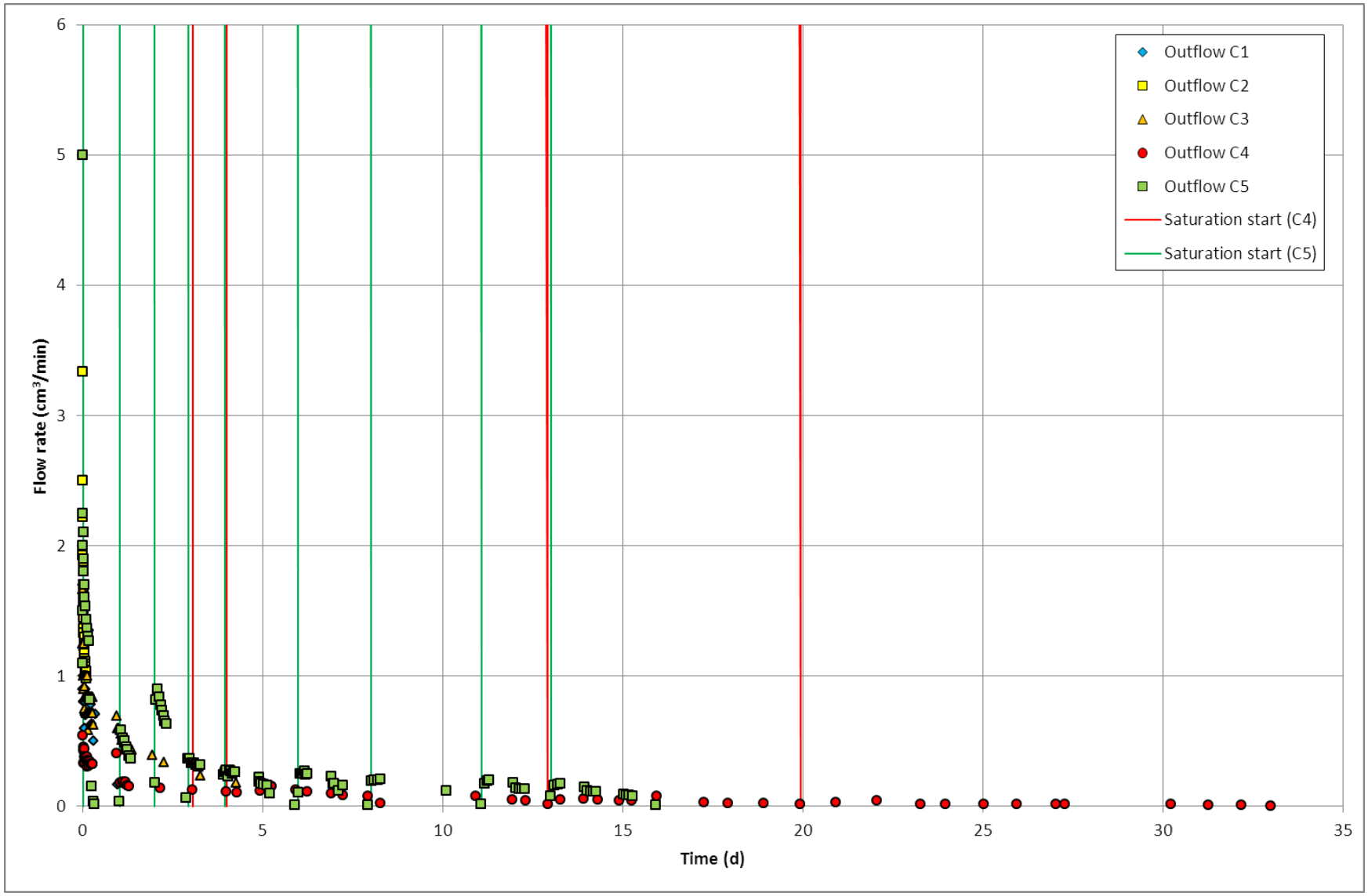
The evolution of flow rate through time in the five soil-column experiments is presented in detail for 1.4 days in Graph 6, and for the whole time length of the experiment and pore-volume in Graph 7 and Graph 8, respectively.

Flow rate tends to naturally decrease over time, mainly in the first 2.4 to 4.8 hours (0.1 to 0.2 days). After this period, the flow rate continues to decrease but not so fast. It is also observed that flow rate and velocity keep decreasing over time at slightly lower rates. The lower flow rates were observed for column 4 (0.04 $cm^3$/min) at the end of $4^{th}$ cycle of saturation/unsaturation, and completely clogged at the end of 33 day of functioning. However, at every injection pulse, the flow rate temporarily increases, due to the increase of the water hydraulic gradient above the soil top. This is most noticeable in Column 5, that runs for 16 days with 9 saturation/unsaturation cycles (due to its higher permeability), but the last measured flow rates were 0.006 $cm^3$/min, before experiment was stopped.

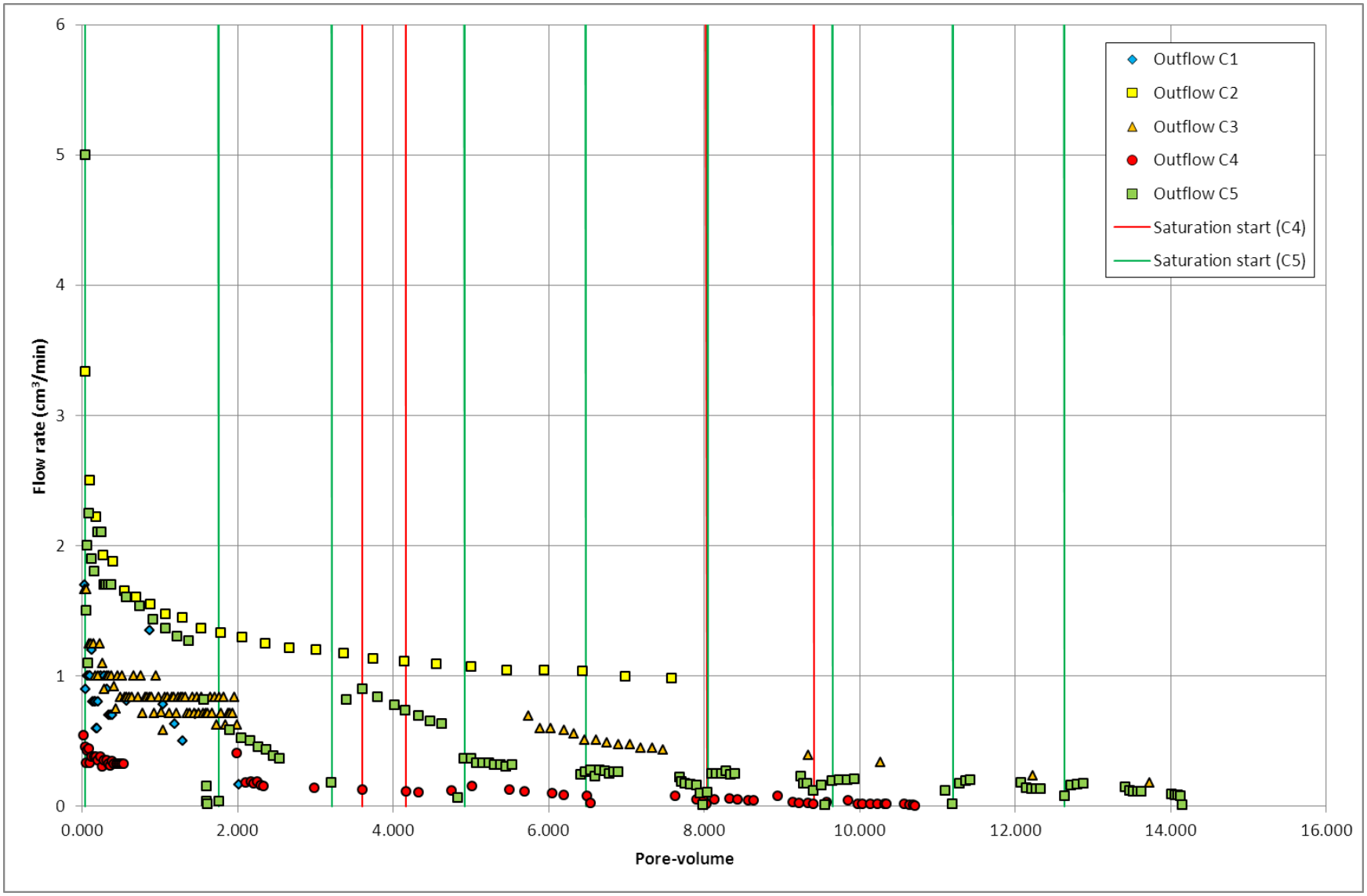
Ponding above soil top was also longer as permeability decreased and time between cycles increased.




**Graph 6 – Natural soil hydraulic behaviour (Time vs Flow rate) – 1.4 days**




**Graph 7 – Natural soil hydraulic behaviour (Time vs Flow rate) – 35 days**




**Graph 8 - Natural soil hydraulic behaviour (Pore-volume vs Flow rate)**

Considering pore-volume units (Graph 8) it is possible to observe that flow rate decreases noticeably at 1 to 2 pore-volumes (0.5 in Column 4), and tend to achieve the lowest values at 14 pore-volumes (equivalent to approximately 3500 mL) (11 pore-volumes in Column 4).

As stated previously, clogging processes occurred inside the columns. The large organic and biological load of wastewater will result in the formation of biofilms on the top of the column and in biological activity will be more important inside the column itself - Figure 23. Although the main consequence is a decrease of soil permeability, it can be a positive aspect in biodegrading some contaminants.

**Figure 23 – Biofilm with equal daily cycle in infiltrating water above soil top (Column 4) (left) and biological activity inside the soil column (Column 5) (right)**

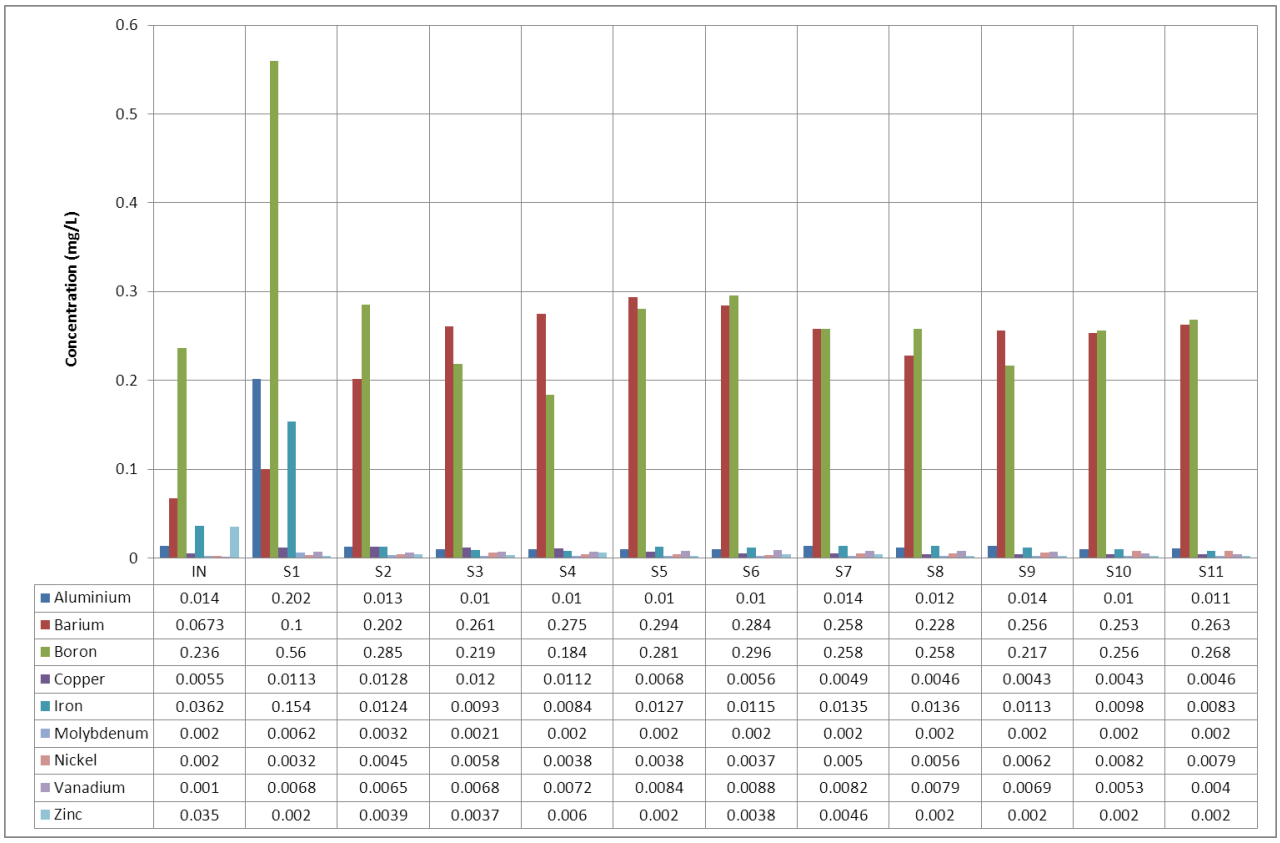
These clogging processes, which are uniquely distributed along the column can create a blockage to water flow at the top section of the column while the bottom section (which has a free flow outlet) continuously desaturates. This can result in different environments inside the column, with lower oxygen on the top and higher on the bottom.

#### *4.3.1.3. Inflow/outflow results comparison*

Soil-column experiment inflow and outflow samples for the SBM natural soil are synthetized in this section. The results were divided into subsections given the type of parameter considered – metals, nitrogen cycle components, major ions and pharmaceuticals. Other parameters that were measured in the outflow in LASUB such as pH, Eh and electrical conductivity are also presented.

#### 4.3.1.3.1. Metals

Metals and metalloids inflow and outflow concentration are presented in Graph 9 to Graph 14 for all three columns (C3, C4 and C5). Considering the large difference in terms of magnitude between these and phosphorous and manganese, they are presented in separate graphs – Column 3 (Graph 10), Column 4 (Graph 12) and Column 5 (Graph 14). It's important to refer that other metals were analysed but only those with values above LOR are presented.



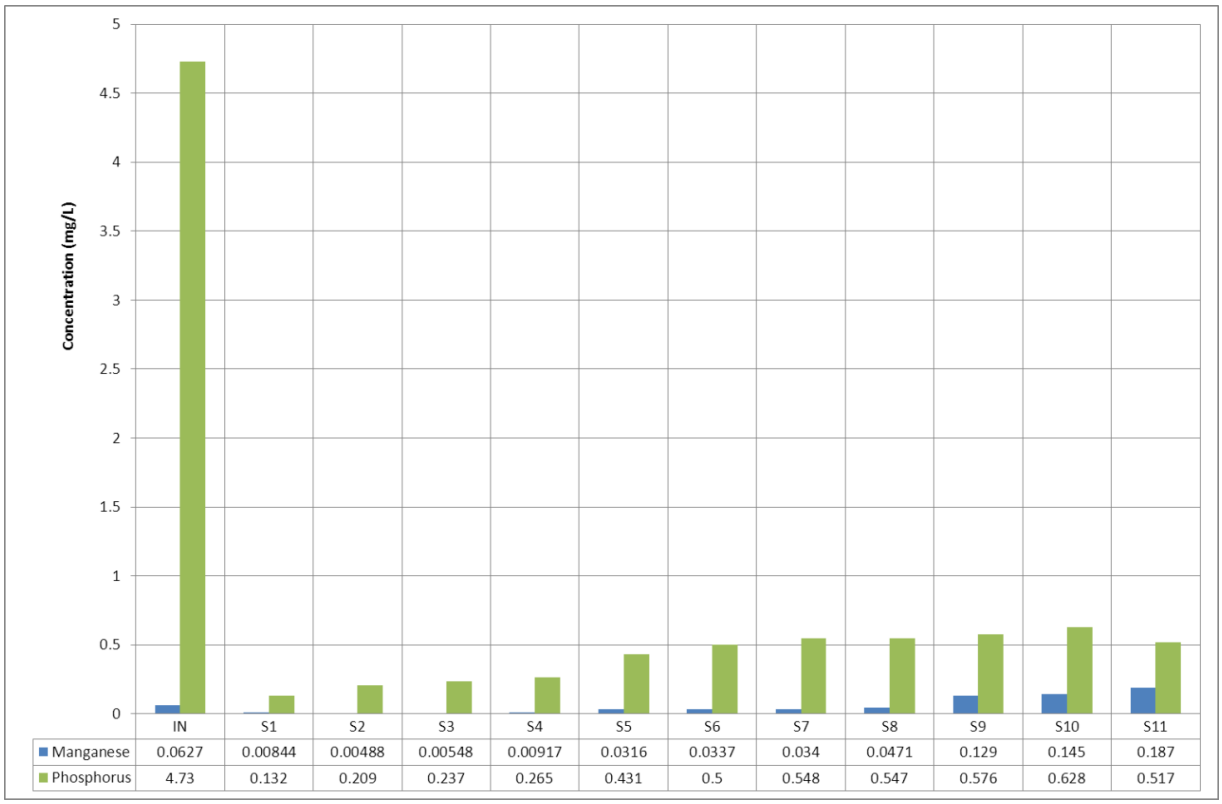

| | IN | S1 | S2 | S3 | S4 | S5 | S6 | S7 | S8 | S9 | S10 | S11 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Aluminium | 0.014 | 0.202 | 0.013 | 0.01 | 0.01 | 0.01 | 0.01 | 0.014 | 0.012 | 0.014 | 0.01 | 0.011 |
| Barium | 0.0673 | 0.1 | 0.202 | 0.261 | 0.275 | 0.294 | 0.284 | 0.258 | 0.228 | 0.256 | 0.253 | 0.263 |
| Boron | 0.236 | 0.56 | 0.285 | 0.219 | 0.184 | 0.281 | 0.296 | 0.258 | 0.258 | 0.217 | 0.256 | 0.268 |
| Copper | 0.0055 | 0.0113 | 0.0128 | 0.012 | 0.0112 | 0.0068 | 0.0056 | 0.0049 | 0.0046 | 0.0043 | 0.0043 | 0.0046 |
| Iron | 0.0362 | 0.154 | 0.0124 | 0.0093 | 0.0084 | 0.0127 | 0.0115 | 0.0135 | 0.0136 | 0.0113 | 0.0098 | 0.0083 |
| Molybdenum | 0.002 | 0.0062 | 0.0032 | 0.0021 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 |
| Nickel | 0.002 | 0.0032 | 0.0045 | 0.0058 | 0.0038 | 0.0038 | 0.0037 | 0.005 | 0.0056 | 0.0062 | 0.0082 | 0.0079 |
| Vanadium | 0.001 | 0.0068 | 0.0065 | 0.0068 | 0.0072 | 0.0084 | 0.0088 | 0.0082 | 0.0079 | 0.0069 | 0.0053 | 0.004 |
| Zinc | 0.035 | 0.002 | 0.0039 | 0.0037 | 0.006 | 0.002 | 0.0038 | 0.0046 | 0.002 | 0.002 | 0.002 | 0.002 |

**Graph 9 – Metals inflow/outflow concentration in Column 3**

Concerning the first set of metals for Column 3 (aluminium, barium, boron, copper, iron, molybdenum, nickel, vanadium and zinc), inflow water (IN) shows that boron and barium are present in the higher concentration. In the first outflow sample (S1), copper, aluminium, iron, barium and boron show concentrations above those measured in inflow water (IN). This is probably the result of the osmosis and desorption processes resulting from the contact between the soil and the distilled water used for the initial saturation. Besides barium and boron, which are present in higher concentrations throughout all the experiment, all remaining elements show the soil high capacity to retain them for the period of the experiment, considering that they are continuously being fed in the input WW. Assuming that no significant reactions occurred in inflow water since the time of sample in SBM WWTP until time of injection, the presence of B and Ba may be the result of continuous soil washing out, showing that barium and boron are very conservative under the existing conditions and maybe also a part of the soil chemical composition itself (since values are higher than the inflow water). This is consistent with the presence of B and Ba measured in the groundwater downgradient the WWTP discharge (cf. Leitão *et al.*, 2014).

Alloway (1990) referred, from experiments with zinc and iron (two other metals present in the inflow water), in a clay soil with organic matter at different pH values, that these metals are more strongly adsorbed to alkaline soils. Given the characteristics of the soil and its composition in bentonite, illite and kaolinite, zinc reduction at outflow can be explained by adsorption at the exchange sites or entrapment in clay lattice.

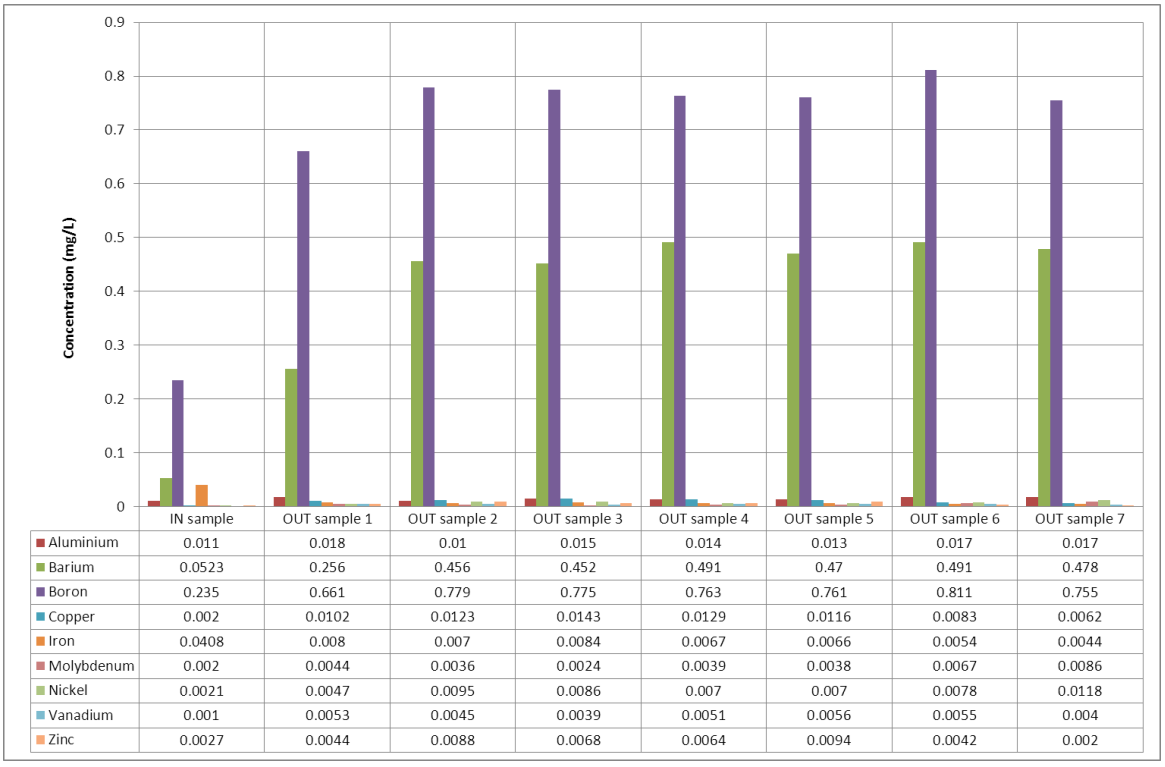
Phosphorous and manganese are other two elements present in the Column 3 inflow water (IN), the first in higher concentration (approximately 5 mg/L) (Graph 10). The first sample (S1) shows that both elements have lower concentration than the inflow, but a trend of increasing in concentration detected on the following samples, although the measured maximum values in outflow are approximately 1/9 of initial concentration for phosphorous. Manganese outflow values are higher than inflow after S9 with increasing trend, corresponding to the soil saturation after approximately 10 pore-volumes.




| | IN | S1 | S2 | S3 | S4 | S5 | S6 | S7 | S8 | S9 | S10 | S11 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Manganese | 0.0627 | 0.00844 | 0.00488 | 0.00548 | 0.00917 | 0.0316 | 0.0337 | 0.034 | 0.0471 | 0.129 | 0.145 | 0.187 |
| Phosphorus | 4.73 | 0.132 | 0.209 | 0.237 | 0.265 | 0.431 | 0.5 | 0.548 | 0.547 | 0.576 | 0.628 | 0.517 |

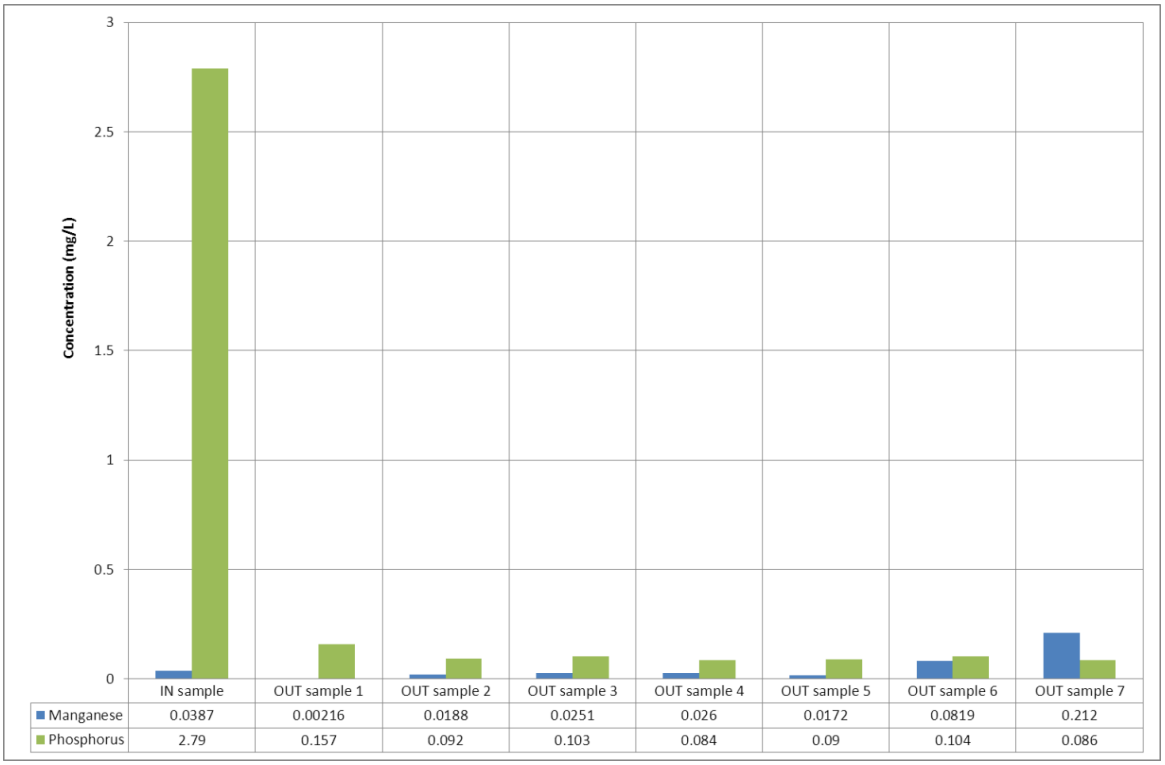
**Graph 10 – Manganese and phosphorus inflow/outflow concentration in Column 3**

Column 4 metals (excluding phosphorous and manganese) in inflow water (IN) show, similarly to C3, that boron, barium and iron are common in this water matrix. All outflow samples show higher concentrations for these elements, except iron. At outflow boron presents almost 3 times the inflow concentration while barium has 10 times the inflow concentration, both with increasing trends until outflow sample 2 and oscillating behaviour after that. Aluminium and molybdenum (which has a below LOR value at inflow) show higher concentration in the first outflow sample but the values remain more or less stable throughout the experiment.




| | IN sample | OUT sample 1 | OUT sample 2 | OUT sample 3 | OUT sample 4 | OUT sample 5 | OUT sample 6 | OUT sample 7 |
|---|---|---|---|---|---|---|---|---|
| Aluminium | 0.011 | 0.018 | 0.01 | 0.015 | 0.014 | 0.013 | 0.017 | 0.017 |
| Barium | 0.0523 | 0.256 | 0.456 | 0.452 | 0.491 | 0.47 | 0.491 | 0.478 |
| Boron | 0.235 | 0.661 | 0.779 | 0.775 | 0.763 | 0.761 | 0.811 | 0.755 |
| Copper | 0.002 | 0.0102 | 0.0123 | 0.0143 | 0.0129 | 0.0116 | 0.0083 | 0.0062 |
| Iron | 0.0408 | 0.008 | 0.007 | 0.0084 | 0.0067 | 0.0066 | 0.0054 | 0.0044 |
| Molybdenum | 0.002 | 0.0044 | 0.0036 | 0.0024 | 0.0039 | 0.0038 | 0.0067 | 0.0086 |
| Nickel | 0.0021 | 0.0047 | 0.0095 | 0.0086 | 0.007 | 0.007 | 0.0078 | 0.0118 |
| Vanadium | 0.001 | 0.0053 | 0.0045 | 0.0039 | 0.0051 | 0.0056 | 0.0055 | 0.004 |
| Zinc | 0.0027 | 0.0044 | 0.0088 | 0.0068 | 0.0064 | 0.0094 | 0.0042 | 0.002 |

**Graph 11 – Metals inflow/outflow concentration in Column 4**

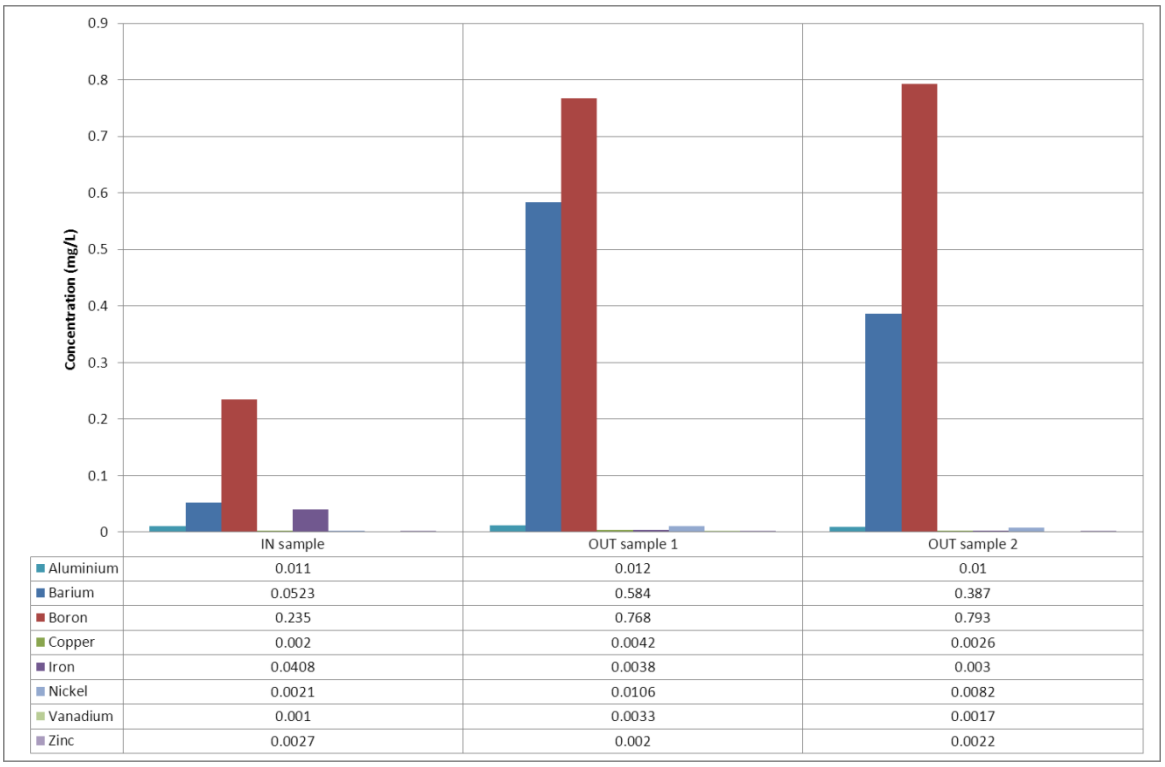



| | IN sample | OUT sample 1 | OUT sample 2 | OUT sample 3 | OUT sample 4 | OUT sample 5 | OUT sample 6 | OUT sample 7 |
|---|---|---|---|---|---|---|---|---|
| Manganese | 0.0387 | 0.00216 | 0.0188 | 0.0251 | 0.026 | 0.0172 | 0.0819 | 0.212 |
| Phosphorus | 2.79 | 0.157 | 0.092 | 0.103 | 0.084 | 0.09 | 0.104 | 0.086 |

**Graph 12 – Manganese and phosphorus inflow/outflow concentration in Column 4**

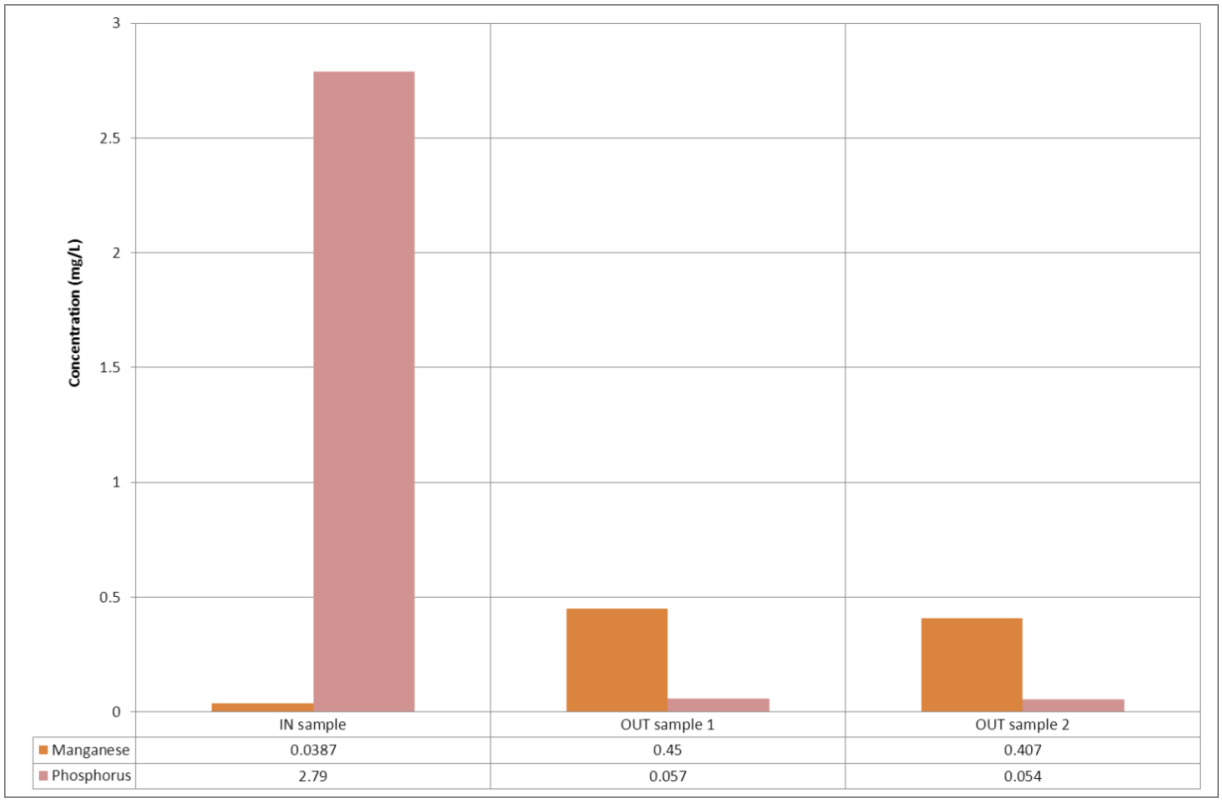
Concerning manganese and phosphorus, the behaviour is very similar to Column 3. Phosphorus outflow concentration is much smaller than inflow and shows an oscillating behaviour, while manganese shows lower outflow concentration at the first until sample five and from there a trend to increasing concentration, higher than inflow due to soil saturation.

Column 5 inflow water present similar results than Column 4, being boron, barium and iron the noticeable concentrations. Outflow samples also present higher concentrations for boron and barium, although the second element shows a decrease between Sample 1 and Sample 2. Besides this, the number of samples does not allow for establishing a trend. Nickel shows higher concentration in both outflow samples when compared to inflow. Molybdenum is not presented as none of the samples (both inflow and outflow) are above LOR.




| | IN sample | OUT sample 1 | OUT sample 2 |
|---|---|---|---|
| Aluminium | 0.011 | 0.012 | 0.01 |
| Barium | 0.0523 | 0.584 | 0.387 |
| Boron | 0.235 | 0.768 | 0.793 |
| Copper | 0.002 | 0.0042 | 0.0026 |
| Iron | 0.0408 | 0.0038 | 0.003 |
| Nickel | 0.0021 | 0.0106 | 0.0082 |
| Vanadium | 0.001 | 0.0033 | 0.0017 |
| Zinc | 0.0027 | 0.002 | 0.0022 |

**Graph 13 – Metals inflow/outflow concentration in Column 5**

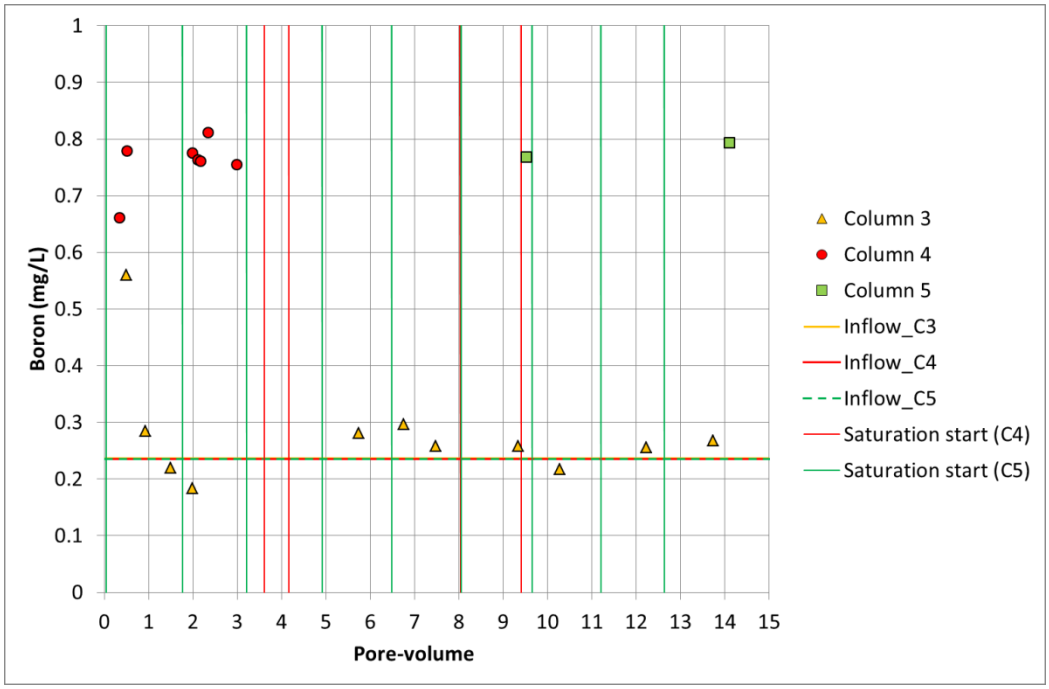



**Graph 14 – Manganese and phosphorus inflow/outflow concentration in Column 5**

Column 5 outflow results for manganese and phosphorous again show similar behaviour to Column 4, as phosphorous decreases in outflow and manganese presents higher outflow concentration when compared with inflow. Soil washing out may be the cause for this behaviour.

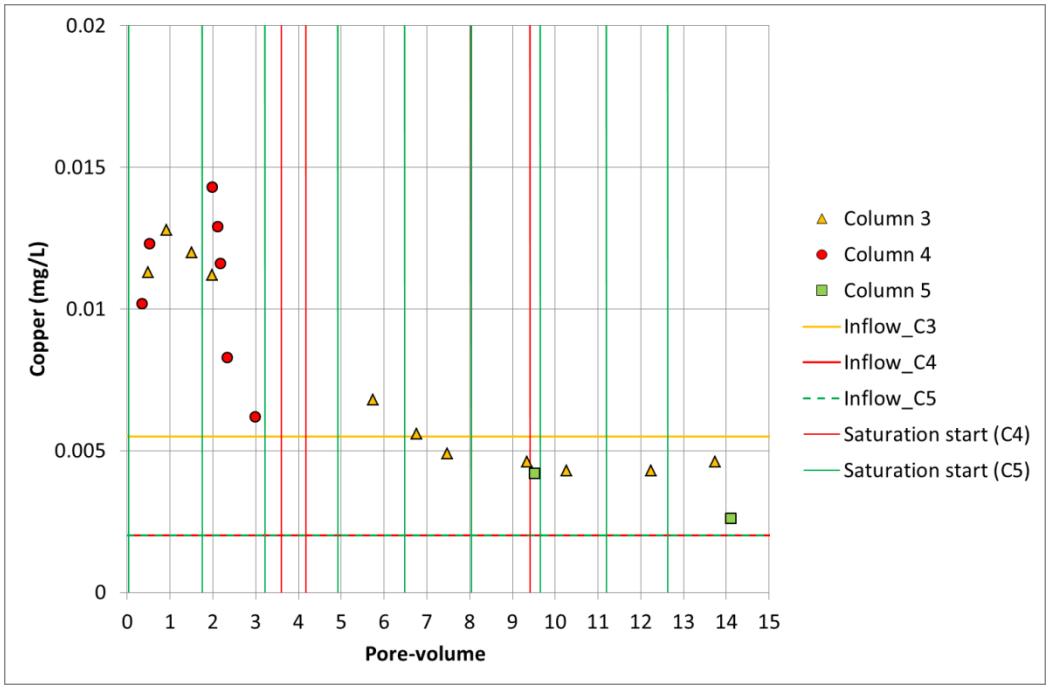
Given the inflow water matrix (wastewater), a particular attention was given to three metals that may be considered tracers and common – boron, copper and zinc. Concentration variations along the experiment for these elements are presented in terms of natural soil pore-volume units in Graph 15 to Graph 17.

Boron conservative behaviour is observed in detail, particularly in Column 3 where concentration at outflow remains very stable along al the experiment (although oscillating), and approximately the same as inflow (Graph 15). Column 4 and Column 5 both present higher concentrations of boron at outflow, but similar values. Saturation and non-saturation conditions show no effect on B concentration.



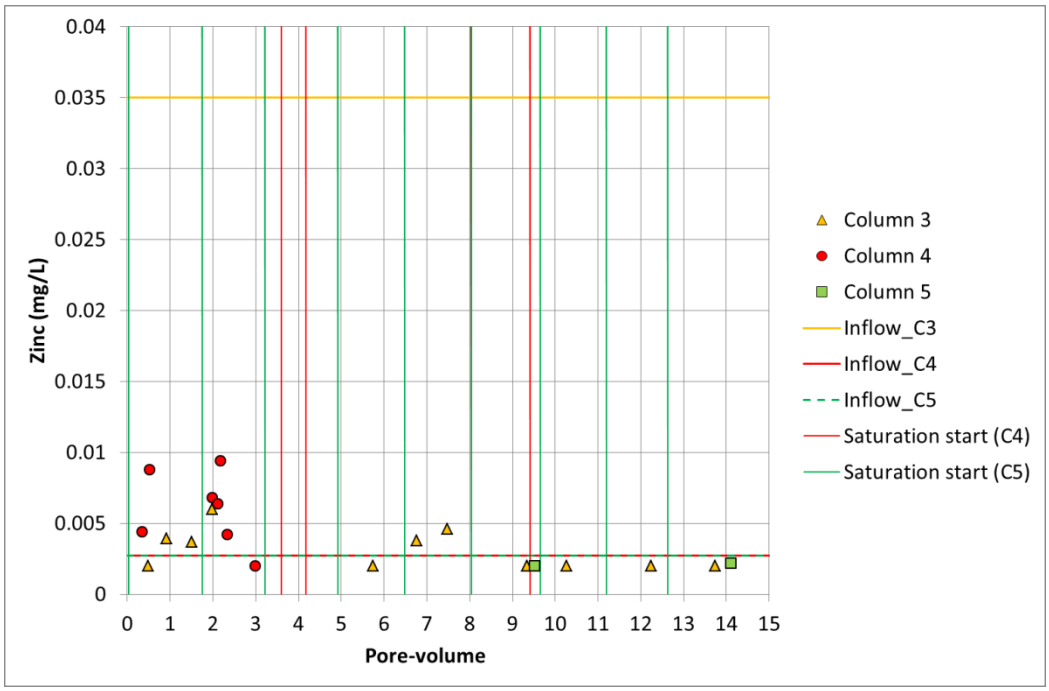

**Graph 15 - Boron vs pore-volume (natural soil)**

Copper is show similar behaviour between Column 3 and Column 4 (Graph 16), with an increase of concentration at outflow between the first and second pore-volume and a steady decrease after that, suggesting a soil washing out process for this element, which origin is due to the soil composition and not to the WW. Column 5 number of samples does not allow for any complex conclusions other than that in pore-volume (PV) 9 and PV14 copper concentrations is still at higher concentrations than the inflow. The slow decrease in concentration at outflow can be explained by the fact that Cu is specifically adsorbed by soil at relatively slow rates (Alloway, 1990), being the retention process very ineffective on the first stages of the experiments.




**Graph 16 – Copper vs Pore-volume (natural soil)**

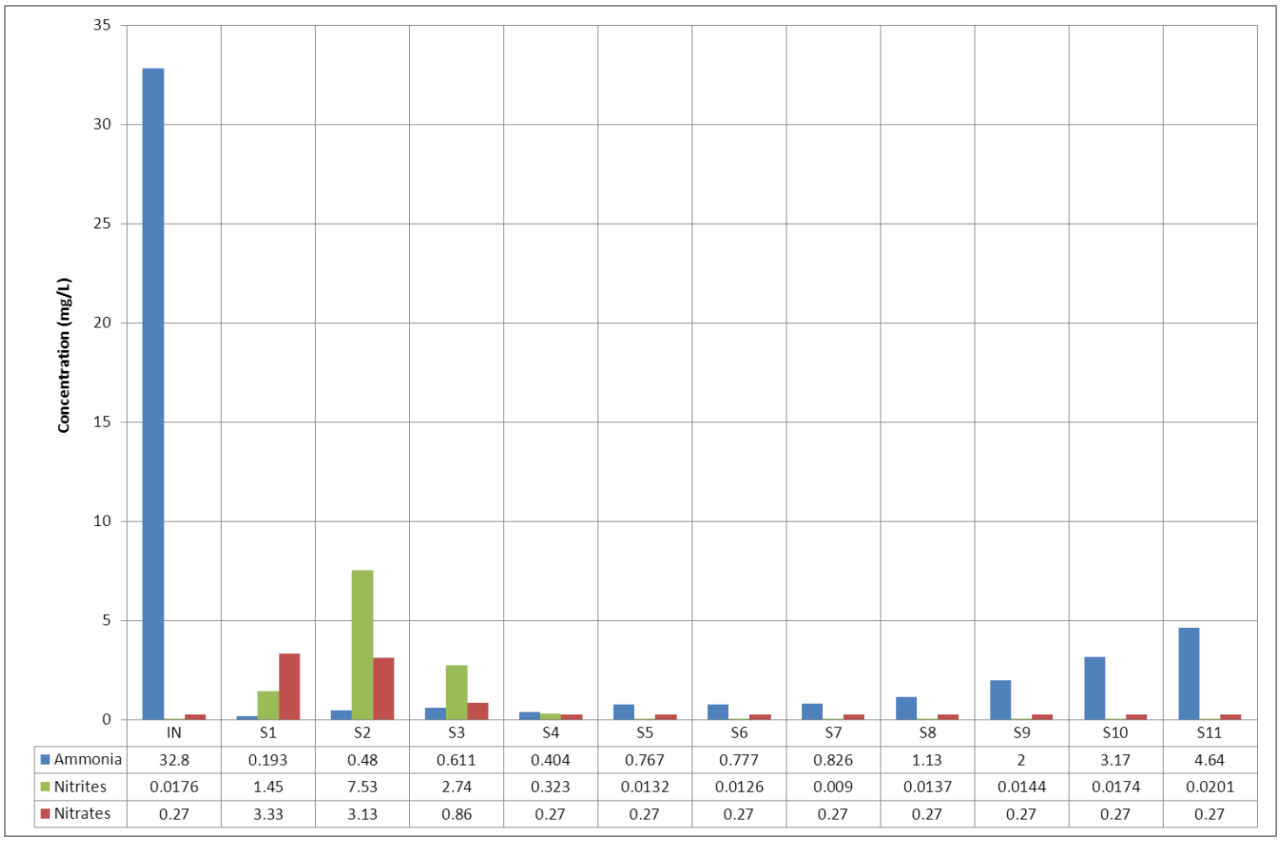
Finally zinc show an oscillating behaviour along C3 experiment with values always below injection concentration. Column 4 shows an irregular behaviour, with zinc concentration increasing irregularly after experiment start and PV2-3 and an outflow concentration below inflow at PV3. Again C5 results only allow establishing that at PV 9 and PV14 values of zinc are below inflow concentration in similar behaviour to C3 results.




**Graph 17 – Zinc vs Pore-volume (natural soil)**

#### 4.3.1.3.2. Nitrogen cycle

The results of ammonia, nitrites and nitrates concentrations are presented for Column 3, Column 4 and Column 5 in Graph 18, Graph 19 and Graph 20, respectively.

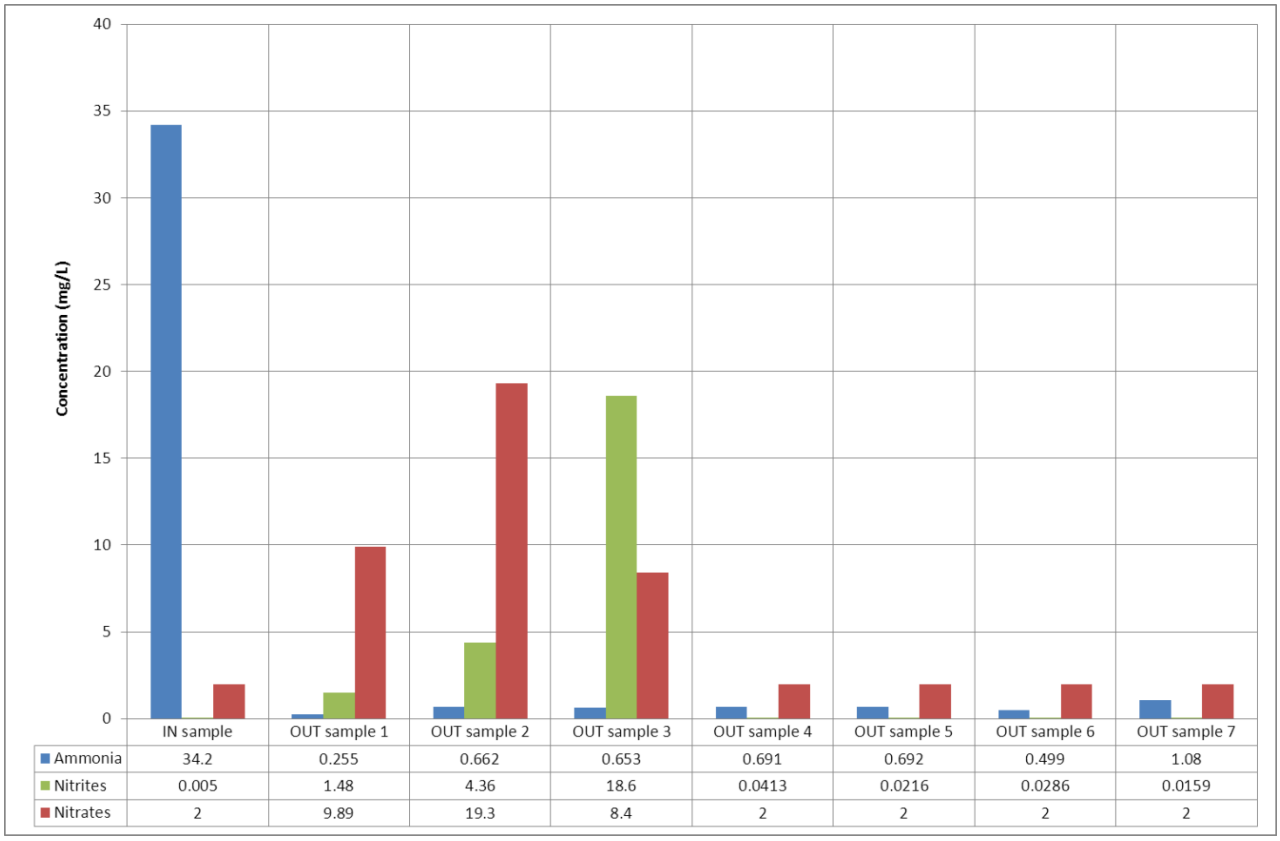



| | IN | S1 | S2 | S3 | S4 | S5 | S6 | S7 | S8 | S9 | S10 | S11 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ammonia | 32.8 | 0.193 | 0.48 | 0.611 | 0.404 | 0.767 | 0.777 | 0.826 | 1.13 | 2 | 3.17 | 4.64 |
| Nitrites | 0.0176 | 1.45 | 7.53 | 2.74 | 0.323 | 0.0132 | 0.0126 | 0.009 | 0.0137 | 0.0144 | 0.0174 | 0.0201 |
| Nitrates | 0.27 | 3.33 | 3.13 | 0.86 | 0.27 | 0.27 | 0.27 | 0.27 | 0.27 | 0.27 | 0.27 | 0.27 |

**Graph 18 – Nitrogen cycle components concentration in Column 3 inflow/outflow**

Column 3 outflow results show an increase in ammonia concentration (although smaller than inflow concentration) along the time the experiment was conducted, while nitrites show an increase on S1 and S2 and a continuous decrease in the next samples. Nitrates also show a higher concentration at S1 when compared to inflow (IN) but the concentration decreases in S2 and S3 until below LOR. In this case, a degradation of ammonia into nitrites and nitrates seem to have occurred in the column, although the total nitrogen at inflow is higher than the measured nitrogen at outflow.

The trend of increasing ammonia in the outflow may have resulted from the fact that continuous injection on Column 3 did not allowed for the column to achieve an aerobic environment, resulting in the formation or non-degradation of injected ammonia.

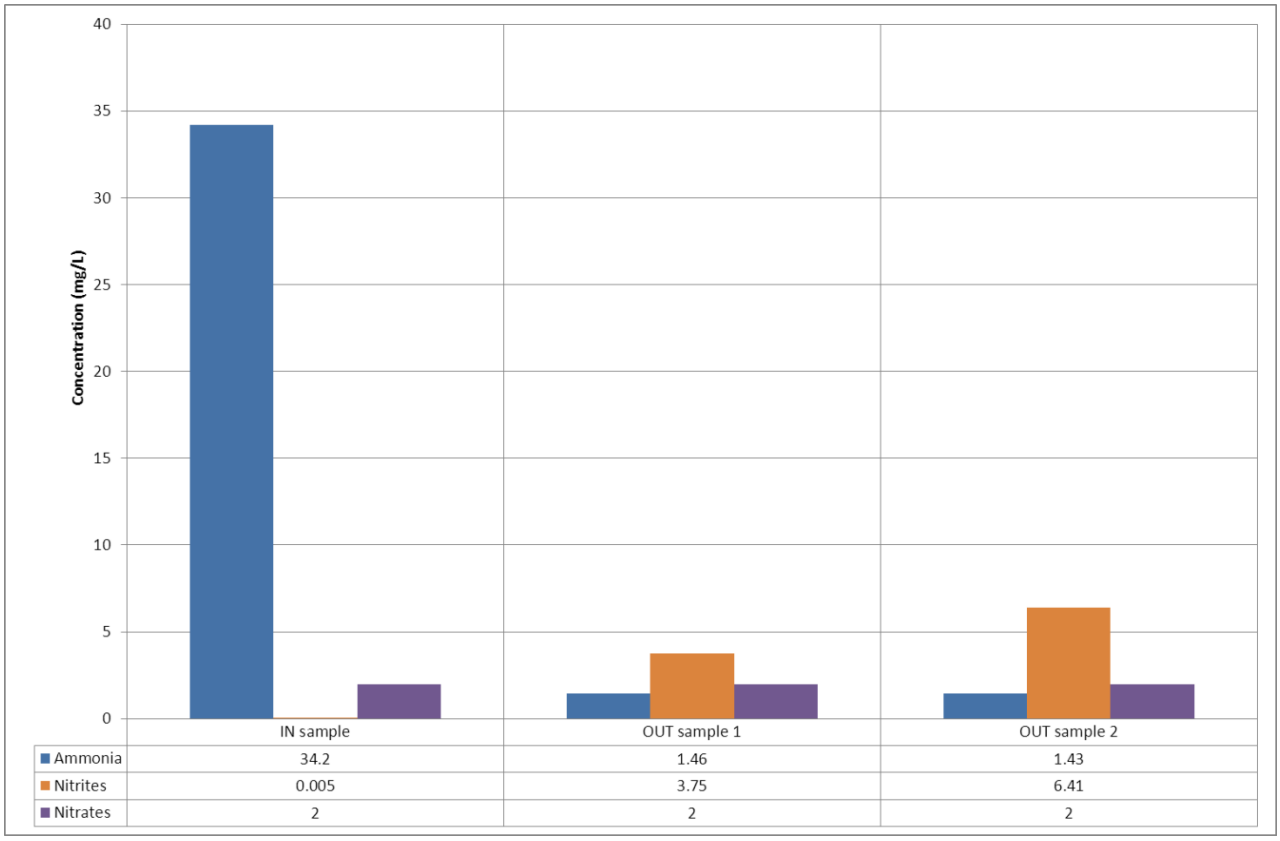



| | IN sample | OUT sample 1 | OUT sample 2 | OUT sample 3 | OUT sample 4 | OUT sample 5 | OUT sample 6 | OUT sample 7 |
|---|---|---|---|---|---|---|---|---|
| Ammonia | 34.2 | 0.255 | 0.662 | 0.653 | 0.691 | 0.692 | 0.499 | 1.08 |
| Nitrites | 0.005 | 1.48 | 4.36 | 18.6 | 0.0413 | 0.0216 | 0.0286 | 0.0159 |
| Nitrates | 2 | 9.89 | 19.3 | 8.4 | 2 | 2 | 2 | 2 |

**Graph 19 – Nitrogen cycle components concentration in Column 4 inflow/outflow**

Column 4 inflow sample show similar composition to Column 3, as ammonia is the predominant compound in the nitrogen cycle. Nitrites and nitrates are in this inflow sample below LOR. After experiment start it's noticeable that ammonia has a very small concentration at OUT sample 1 when compared to inflow, but shows in the following outflow samples a trend for increase. Concerning nitrites, although concentration at outflow is higher than inflow between outflow samples 1 to 3 with an increasing trend, in outflow sample 4 and the next the values highly decrease (from 18.6 mg/L in sample 3 to 0.0413 mg/L in sample 4). A similar behaviour is verified for nitrates concentration, with a peak at outflow sample 2 followed by a steep decrease until values below LOR (OUT sample 4 and next). This may mark a change in the column environment.

Again, the slight increase of ammonia along the experiment may represent that each cycle is less successful in oxygenating the column. This may be due to clogging processes inside the column that keep the column always saturated even with oxygenation (no injection) periods. Also, as permeability decreases, the ponding time above the soil column is longer (see Section 4.3.1.2) not allowing for the column to "breath", creating conditions for a redox environment.




**Graph 20 – Nitrogen cycle components concentration in Column 5 inflow/outflow**

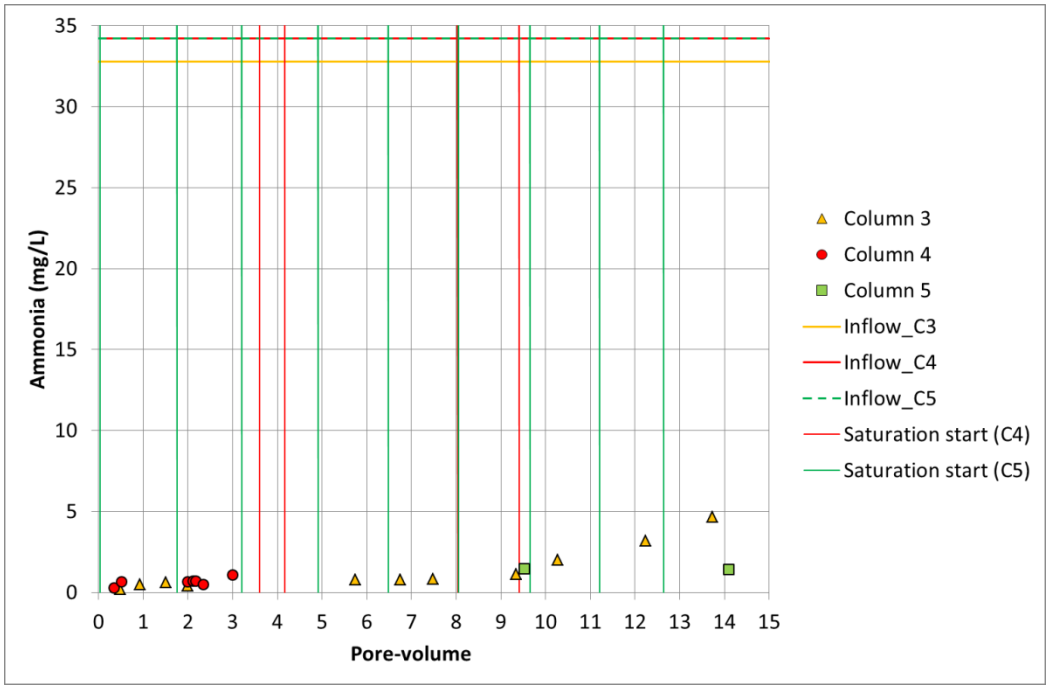
Finally, column 5 inflow show similar composition to Column 4, and an increase in nitrites in the following 2 samples collected from the outflow. Nitrates remained below LOR while ammonia showed again a decrease in concentration when compared to inflow.

Visualizing the behaviour of these tree elements along the experiment in terms of pore-volume may be helpful to understand it. Ammonia, nitrites and nitrates are presented in Graph 21, Graph 22 and Graph 23, respectively.

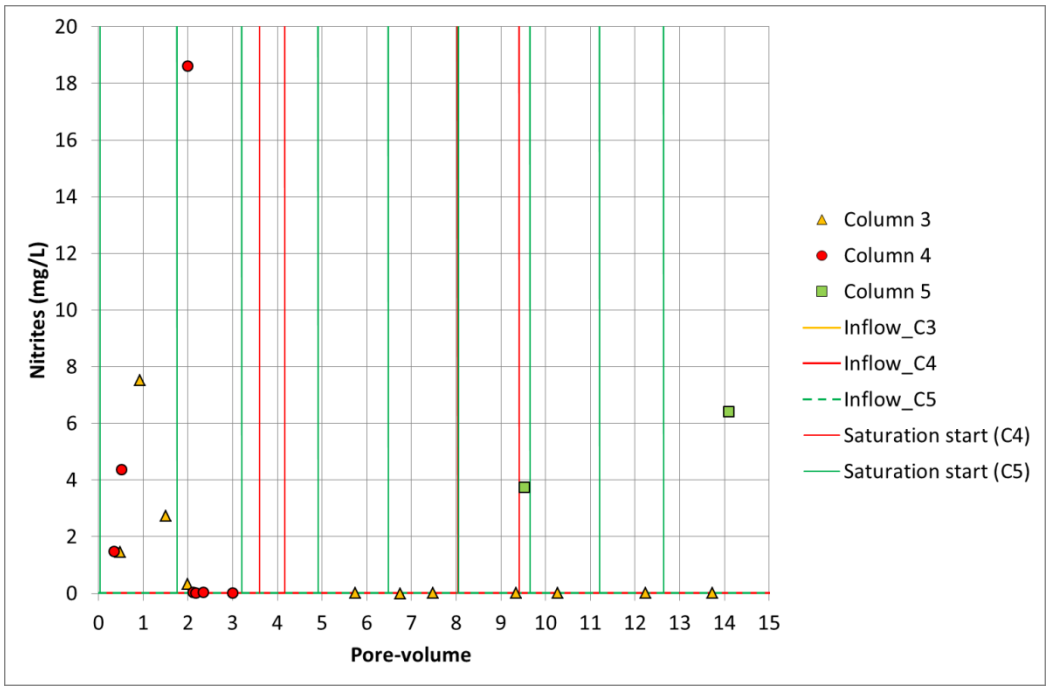
Concerning ammonia, Column 3 presents a steady concentration below inflow until approximately PV9 where it starts to gradually increase. Similar behaviour is presented in Column 4, although there is only data until PV3. Values at outflow are very similar between the 3 soil-column experiments.

As stated above, nitrites behave similarly in Column 3 and Column 4 with an increase between PV1 and PV2 and a stable concentration parallel to inflow. Column 5 shows nitrite concentration higher than C3 and C4 at PV9 and PV14.

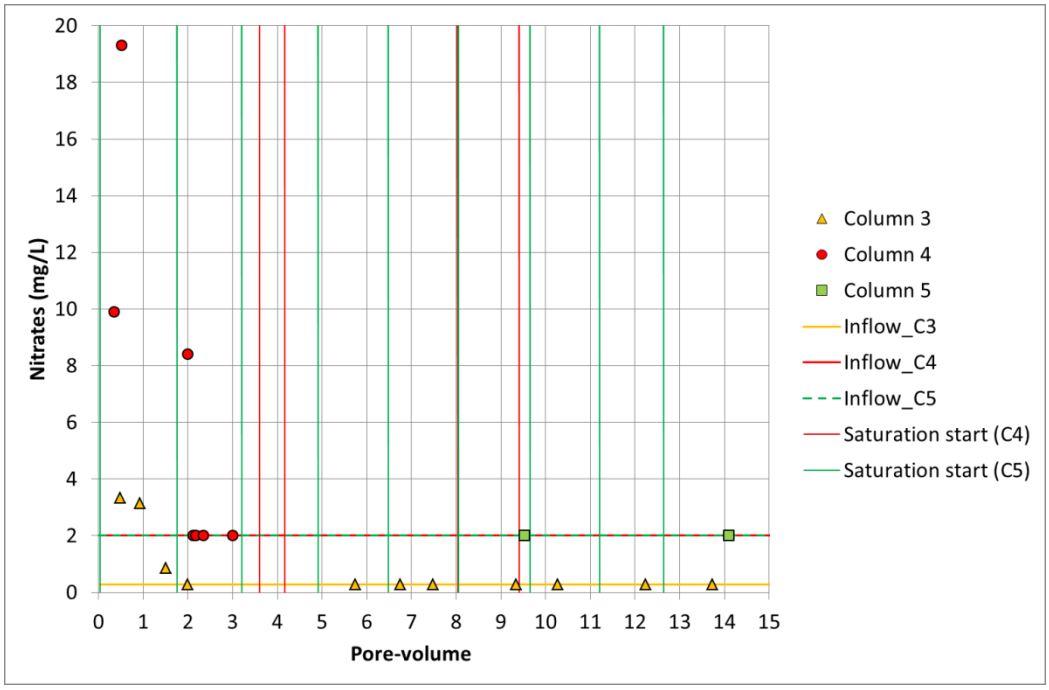
Nitrates only show values above LOR between PV1 and PV2 in both Column 3 and Column 4.




**Graph 21 – Ammonia vs pore-volume (natural soil)**




**Graph 22 – Nitrites vs pore-volume (natural soil)**




**Graph 23 – Nitrates vs pore-volume (natural soil)**

From the analysis of the results of the three columns, it is possible to see that ammonia ($NH_4^+$) is being nitrified in the first pore-volume periods, when nitrites ($NO_2^-$) and nitrates ($NO_3^-$) were increased:

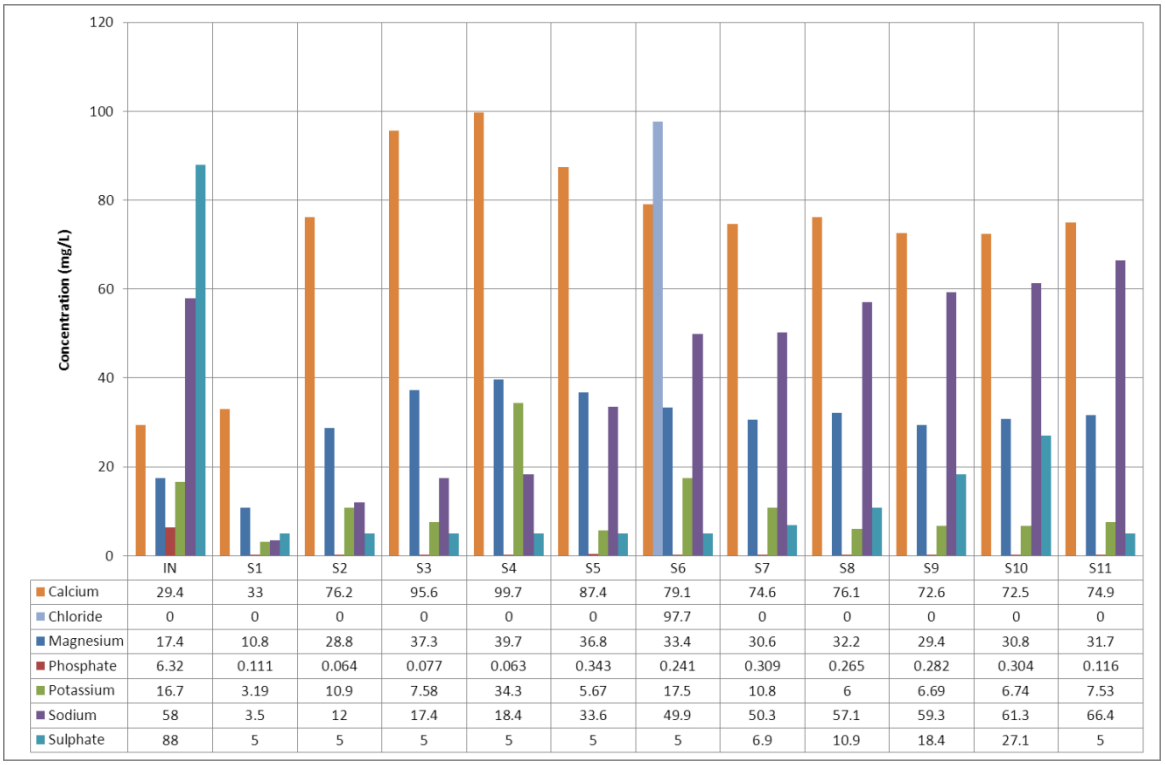
$$2\ NH_4^+ + 3\ O_2 \rightarrow 2\ NO_2^- + 2\ H_2O + 4\ H^+$$

$$2\ NO_2^- + O_2 \rightarrow 2\ NO_3^-$$

This denitrification process was possible throughout the all period of Column 4 and 5 experiments due to the saturation-desaturation sequence imposed. However, Column 3 was saturated all the time; therefore, the absence of $O_2$ did not allow denitrification in the last stages (PV) which resulted in the presence of more $NH_4^+$. These results show the importance of saturation-desaturation cycles in the N cycle degradation.

#### 4.3.1.3.3. Major ions

Results from major ions for Column 3, Column 4 and Column 5 are presented in Graph 24, Graph 25 and Graph 26, respectively. Due to the large required volume, bicarbonate was not analysed.



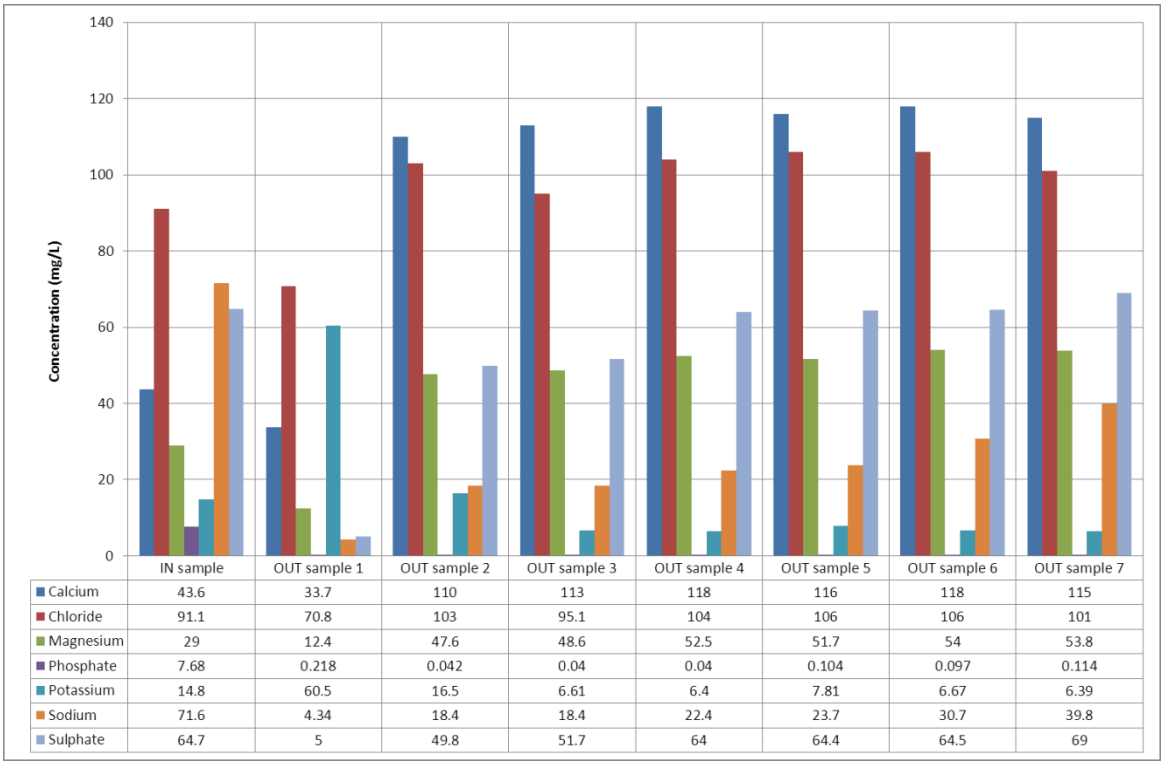

| | IN | S1 | S2 | S3 | S4 | S5 | S6 | S7 | S8 | S9 | S10 | S11 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Calcium | 29.4 | 33 | 76.2 | 95.6 | 99.7 | 87.4 | 79.1 | 74.6 | 76.1 | 72.6 | 72.5 | 74.9 |
| Chloride | 0 | 0 | 0 | 0 | 0 | 0 | 97.7 | 0 | 0 | 0 | 0 | 0 |
| Magnesium | 17.4 | 10.8 | 28.8 | 37.3 | 39.7 | 36.8 | 33.4 | 30.6 | 32.2 | 29.4 | 30.8 | 31.7 |
| Phosphate | 6.32 | 0.111 | 0.064 | 0.077 | 0.063 | 0.343 | 0.241 | 0.309 | 0.265 | 0.282 | 0.304 | 0.116 |
| Potassium | 16.7 | 3.19 | 10.9 | 7.58 | 34.3 | 5.67 | 17.5 | 10.8 | 6 | 6.69 | 6.74 | 7.53 |
| Sodium | 58 | 3.5 | 12 | 17.4 | 18.4 | 33.6 | 49.9 | 50.3 | 57.1 | 59.3 | 61.3 | 66.4 |
| Sulphate | 88 | 5 | 5 | 5 | 5 | 5 | 5 | 6.9 | 10.9 | 18.4 | 27.1 | 5 |

**Graph 24 – Column 3 major ions inflow/outflow concentrations**

Column 3 results concerning major ions allow establishing that inflow water shows that chloride is the only parameter not detected, and sulphate is very abundant followed by sodium and calcium. Sulphate shows lower concentrations at outflow when compared to inflow, while sodium (although similar) show a clear increase trend and surpasses inflow concentration outflow after sample 9 (S9).

Calcium is the most abundant ion at outflow with concentration that is 3 times higher than inflow (S3). After a trend of concentration decrease seems to be established, allowing to assume that this element common in soil concentration is being continuously washed out. Magnesium shows equal behaviour although with lower concentrations, as well as potassium, with some peaks in S4 and S6 and steady behaviour after that.

Chloride behaviour suggest that some problem occurred in the detection of this ion taking into account that concentration goes from 0 mg/L in every sample to 97.9 mg/L in only one sample (S6).

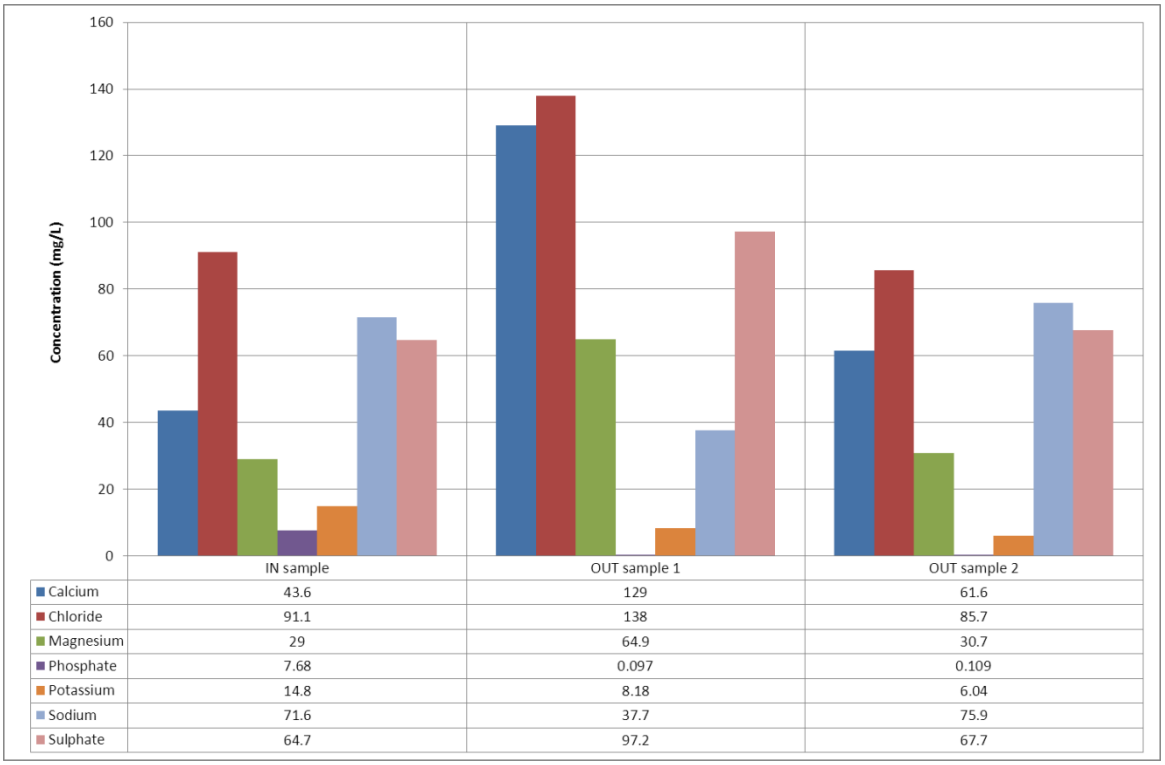



| | IN sample | OUT sample 1 | OUT sample 2 | OUT sample 3 | OUT sample 4 | OUT sample 5 | OUT sample 6 | OUT sample 7 |
|---|---|---|---|---|---|---|---|---|
| Calcium | 43.6 | 33.7 | 110 | 113 | 118 | 116 | 118 | 115 |
| Chloride | 91.1 | 70.8 | 103 | 95.1 | 104 | 106 | 106 | 101 |
| Magnesium | 29 | 12.4 | 47.6 | 48.6 | 52.5 | 51.7 | 54 | 53.8 |
| Phosphate | 7.68 | 0.218 | 0.042 | 0.04 | 0.04 | 0.104 | 0.097 | 0.114 |
| Potassium | 14.8 | 60.5 | 16.5 | 6.61 | 6.4 | 7.81 | 6.67 | 6.39 |
| Sodium | 71.6 | 4.34 | 18.4 | 18.4 | 22.4 | 23.7 | 30.7 | 39.8 |
| Sulphate | 64.7 | 5 | 49.8 | 51.7 | 64 | 64.4 | 64.5 | 69 |

**Graph 25 – Column 4 major ions inflow/outflow concentrations**

Column 4 inflow water shows large concentrations of calcium, chloride, magnesium, potassium, sodium and sulphate above 10 mg/L. Similarly to Column 3, calcium and magnesium show values above inflow concentration at the outflow. Sulphate shows a clear increasing trend to achieve inflow values at outflow sample 7. Similarly sodium shows an increase in concentration throughout the experiment, while potassium remains more or less steady after outflow sample 2, suggesting that this element washing out occurred at this point.

Finally chloride behaviour seems to be similar to calcium and magnesium, and clearly differ with Column 3s inflow/outflow concentrations.




| | IN sample | OUT sample 1 | OUT sample 2 |
|---|---|---|---|
| Calcium | 43.6 | 129 | 61.6 |
| Chloride | 91.1 | 138 | 85.7 |
| Magnesium | 29 | 64.9 | 30.7 |
| Phosphate | 7.68 | 0.097 | 0.109 |
| Potassium | 14.8 | 8.18 | 6.04 |
| Sodium | 71.6 | 37.7 | 75.9 |
| Sulphate | 64.7 | 97.2 | 67.7 |

**Graph 26 – Column 5 major ions inflow/outflow concentrations**

Column 5 shows an increase in sulphate, calcium, magnesium, sodium and chloride, with concentrations values above inflow. Phosphate shows very low concentrations in comparison, and potassium seems to be slowly decreasing in concentration throughout the experiment. Again, continuous washing out of magnesium and calcium is apparently occurring while chloride seems to have a persistent behaviour.

#### 4.3.1.3.4. Pharmaceuticals

The final set of parameters analysed is pharmaceuticals. Although a set of 24 of these compounds were analysed (60 parameters in the case of Column 3), special attention was given to those that were detected in outflow, and are commonly referred in bibliographic references as being persistent.

It's important to refer that pharmaceuticals at inflow where only analysed for Column 4 and Column 5, while in Column 3 only one outflow sample for these compounds was analysed.

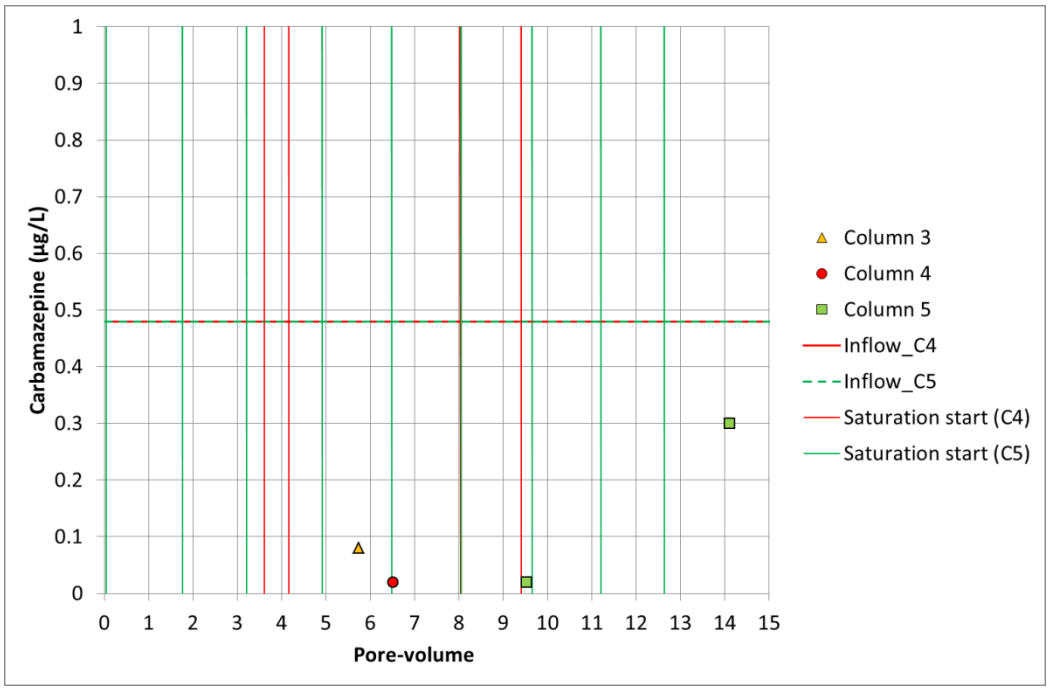
Concerning Column 3, outflow analysis of 60 different compounds showed that carbamazepine, diclofenac, gemfibrozil, hydrochlorothiazide, ibuprofen, levetiracetam, naproxen and primidone are the only above LOR. From these levetiracetam showed the highest concentration (2.1 µg/L) and primidone the lowest (0.02 µg/L).

For Column 4 and Column 5 inflow water pharmaceuticals concentrations please refer to Table 13 in Section 4.2.3.

For the 24 compounds considered in outflow water for Column 4 (1 sample), bezafibrate, carbamazepine diclofenac, gemfibrozil and naproxen showed concentrations above LOR, with the highest being naproxen (0.46 µg/L) and the lowest in carbamazepine (0.02 µg/L).

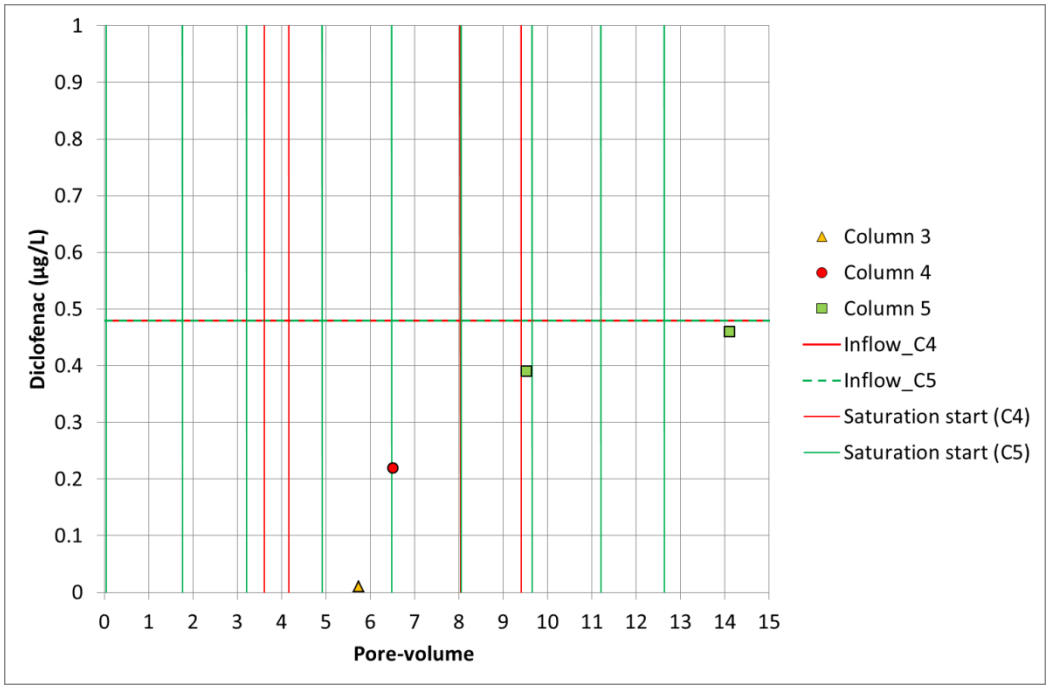
In Column 5, two samples were taken that showed similar results: bezafibrate, carbamazepine, diclofenac, gemfibrozil, ibuprofen and naproxen. Column 5 sample 1 compound with lowest concentration is carbamazepine (0.02 µg/L) and the highest is naproxen (0.76 µg/L). In sample two, naproxen shows again the highest concentration (0.61 µg/L) and ibuprofen the lowest (0.17 µg/L)

Pore-volume progression throughout the experiments is presented for carbamazepine, diclofenac, gemfibrozil and naproxen are presented in Graph 27 to Graph 30.



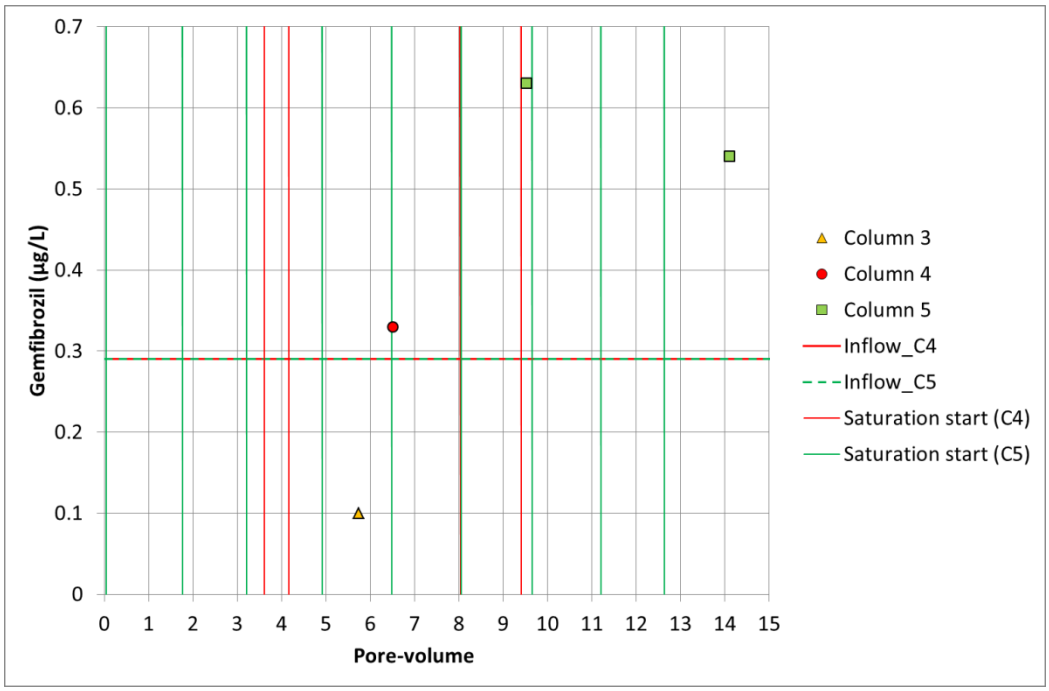

**Graph 27 – Carbamazepine vs pore-volume (natural soil)**

Carbamazepine, although with an increasing trend in column 5 shows a lower concentration than inflow in all outflow samples for all columns.




**Graph 28 – Diclofenac vs pore-volume (natural soil)**

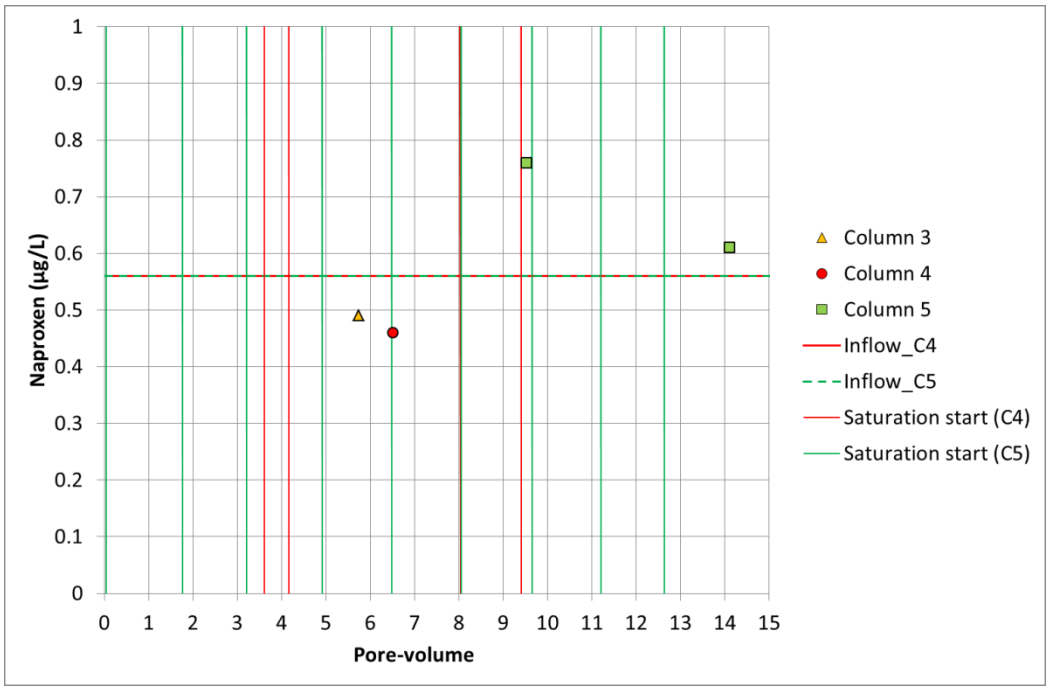
Diclofenac shows similar behaviour as carbamazepine although in Column 5 measured outflow concentrations seem to be converging with inflow concentrations.




**Graph 29 – Gemfibrozil vs pore-volume (natural soil)**

For Column 4 and 5, gemfibrozil was detected in the outflow analysis with higher concentration than inflow. Assuming that no pharmaceuticals are present at the soil, as it is at its natural

state, and that no form of contamination could be possible, this could result from problems with sampling or conditioned retention and washing out when column conditions change. This will be discussed in depth in section 6.1.



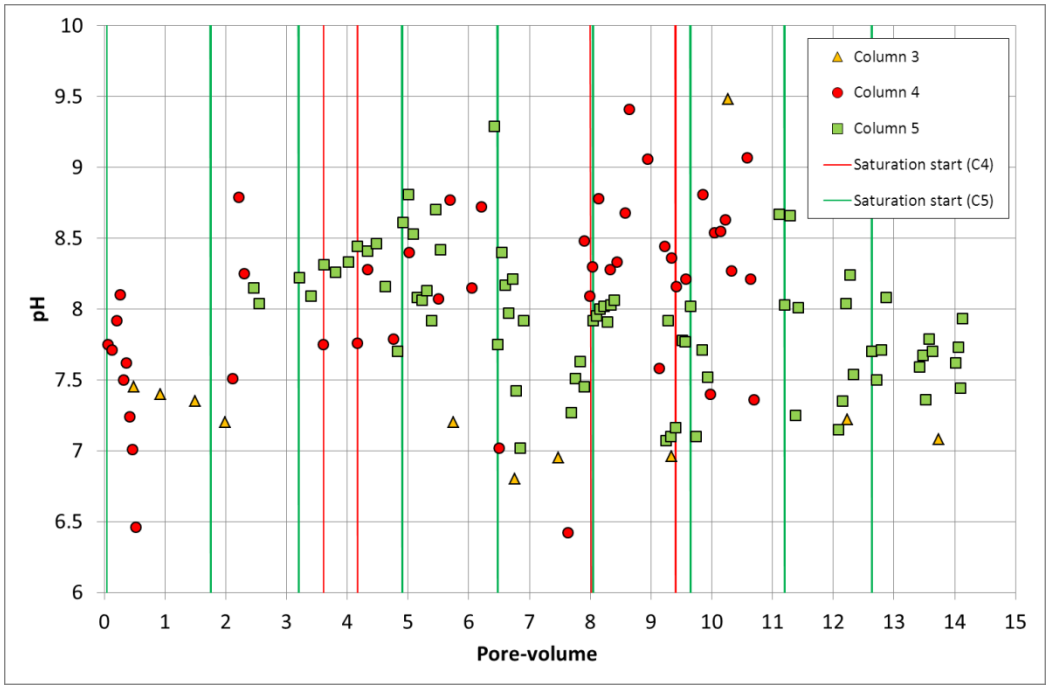

**Graph 30 – Naproxen vs Pore-volume (natural soil)**

Similar behaviour as gemfibrozil was detected in Column 5, with higher outflow concentration when compared with inflow. Column 4 presents a coherent behaviour. Although not presented graphically, ibuprofen outflow concentration values are also higher than inflow.

#### 4.3.1.3.5. pH, Eh and electrical conductivity

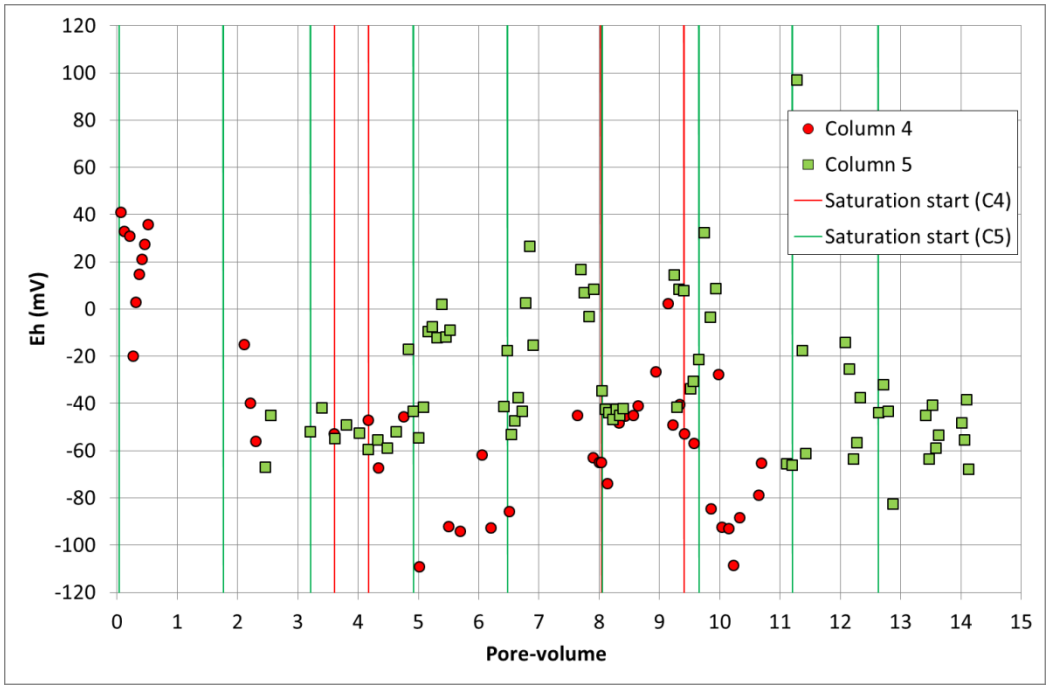
Once a minimum volume for measurement (approximately 15 mL) was collected, pH, redox potential (Eh) and electrical conductivity were recorded. Eh was not measured in Column 3 due to a problem in the sensor. pH, Eh and electrical conductivity are presented in Graph 31, Graph 32 and Graph 33, respectively.

Considering as reference the pH values of Column 3 inflow water (Table 12), which correspond to a slightly acid water (6.08), outflow shows higher values (approximately 7), except in PV10 where it has basic pH (approximately 9.5). Column 4 and Column 5 have a pH of 7.61 at inflow but, with the exception of some samples (in PV0-1 PV6-7 and PV7-8 for Column 4), outflow water for both columns is neutral to basic. In terms of general behaviour although values are very disperse between 6.5 to 9.5 interval, there are no noticeable trends or any variations due to infiltration cycle start. The high pH levels contribute to the retention of most heavy metals in soils (cf. section 4.3.1.3.1) due to the complexes formed with the carbonates and oxides and hydroxides.




**Graph 31 - pH vs pore-volume (natural soil)**

Redox potential analysis (Graph 32) may be the key to understanding the behaviour of certain elements as the redox environment inside the column will facilitate other reactions that can result in degradation/sorption of contaminants.

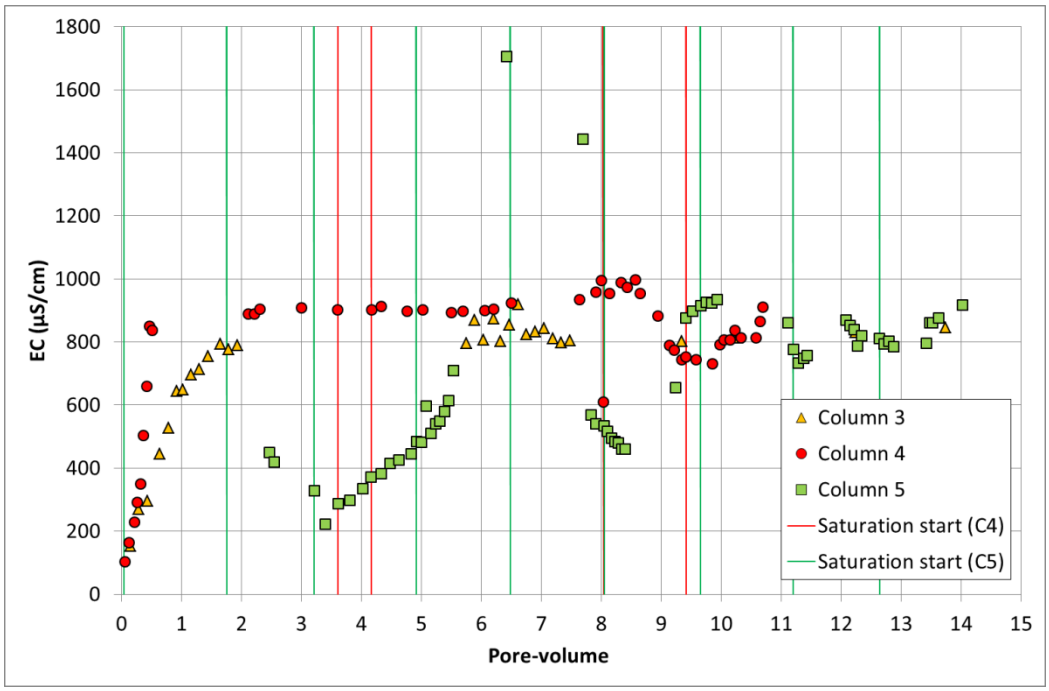



**Graph 32 – Redox potential vs Pore-volume (natural soil)**

Table 12 presents the Eh inflow values for Column 4 and Column 5 (173 mV).

For both Column 4 and Column 5 redox potential values taken at outflow show anaerobic conditions in several occasions, with most of Eh < 40 mV. Column 4 shows a gradual decrease trend in Eh from positive (≈40 mV) to negative values. In Column 5, Eh values remain in the same interval as Column 4 both the lower boundary of interval has higher values. This difference may reflect the success of the saturation/unsaturation cycles in oxygenating the columns, in lower degree in Column 4 that has lower conductivity (see Section 4.3.1.2). In most situations it is possible to observe an increase in the Eh after saturation starts.

Finally, electrical conductivity values (Graph 33) at inflow (760 µS/cm for C3 and 649 µS/cm for C4 and C5) are generally lower than those observed at outflow with the exception of Column 5. At the start of soil-column experiment 3 and 4 it's noticeable an increase of electrical conductivity in outflow that goes to PV1 in C4 and to PV2 in C3. Mixing between deionized water and wastewater is clear at this interval. Considering that wastewater injection in C5 started after 2 cycles of deionized water, the same as C3 and C4 behaviour is observed but only at PV3.




**Graph 33 – Electrical conductivity vs pore-volume (natural soil)**

The continuous washing out process (possibly of Ca and Mg) is observed clearly in Column 4, as electrical conductivity values remain stable after PV1 with only small fluctuation. Similar behaviour is show in Column 3 with electrical conductivity stabilizing between 800 and 900 µS/cm along the experiment after PV2.

Soil in column 5, after PV3 seems to respond to the deionized water/wastewater mixing process. After that, there is a rapid response to wastewater inflow is observed (PV6-7) at saturation cycle start and a following stabilization of behaviour with small fluctuation at each new cycle.

#### *4.3.1.4. Soil analysis*

At the end of the experiment conducted in Column 3 and Column 5, each column was dismantled and soil samples were collected and sent to analysis in an external laboratory. The parameters analysed considered not only pharmaceuticals but also some metals, and nitrogen cycle components. Both columns were split into two equal sections (15 cm each), corresponding to top and bottom. A set of pharmaceutical compounds were analysed for both columns. For these compounds only one composite sample of the soil was considered for Column 3 while for Column 5 two samples were analysed (more precisely, one for the top section and one for the bottom section).

The main results for Column 3 and Column 5 (excluding pharmaceuticals) are presented in Table 19 and Table 20, respectively.

**Table 19 – Column 3 soil analysis results**

| Parameter | Unit | LOR | Sample 1 (top section) | Section 2 (bottom section) |
|---|---|---|---|---|
| Boron | mg/kg DW | 1.0 | 13.4 | 15.4 |
| Copper | mg/kg DW | 1.0 | 32.2 | 33.3 |
| Zinc | mg/kg DW | 3.0 | 30.4 | 31.2 |
| Ammonia | mg/kg DW | 0.50 | 60.3 | 19.8 |
| Nitrates | mg/kg DW | 20 | < 20 | < 20 |
| Nitrites | mg/kg DW | 0.050 | 0.248 | 0.238 |
| Phosphorus | % DW | 0.050 | 0.267 | 0.235 |
| Phosphates | % DW | 0.10 | 0.61 | 0.54 |
| Sulphate | % DW | 0.10 | 0.12 | < 0.10 |

Note: DW – dry weight

The data presented for Column 3 show an almost equal concentration of boron, copper and zinc in top and bottom section, but boron concentrations are clearly lower (although inflow SBM WWTP effluent has higher concentrations in B, cf. Table 12). This confirms the ability of natural soils to retain the Cu and Zn that is continuously fed during the experiment (3 pore-volumes) and the conservative behaviour observed for B that is not retained but leached. Cu and Zn concentrations in soils show a similar value to the average sedimentary soils of the world (30 mg/kg) (Alloway, 1990).

Concerning the nitrogen cycle, ammonia showed much higher concentrations when compared with nitrates and nitrites. Nitrates where not detected in both top or bottom section and nitrites show very small concentration when compared to ammonia in both sections. This seems to justify the large decrease difference between inflow and outflow concentrations verified in all columns, showing that ammonia is heavily retained on the soil top section, besides being transformed into nitrites and nitrates. This last one is conservative, being leached by the outflow water.

Phosphorous and phosphates show higher concentrations in the soil top section but both in small concentrations. This complies with what was verified in outflow water, with relatively important phosphorous concentrations. Sulphate concentration was not detected at bottom section, and on top it was slightly above LOR.

From the set of selected pharmaceuticals, none showed concentrations above LOR. Extended Column 3 soil analysis results are presented in Appendix 3.

Boron and copper in Column 5 (Table 20) showed similar concentrations, although slightly lower, to those detected in Column 3. This is relevant since Column 5 had 15 PV of WW passing through the soil, and the retention capacity for Cu was maintained. Zinc appears to have been concentrated on the bottom section of the column, possibly due to higher saturation.

**Table 20 – Column 5 soil analysis results**

| Parameter | Unit | LOR | Sample 1 (top section) | Section 2 (bottom section) |
|---|---|---|---|---|
| Boron | mg/kg DW | 1.0 | 11.8 | 9.2 |
| Copper | mg/kg DW | 1.0 | 30.1 | 34.3 |
| Zinc | mg/kg DW | 3.0 | 27.4 | 48 |
| Ammonia | mg/kg DW | 0.50 | 71.2 | 17.6 |
| Nitrates | mg/kg DW | 20 | 140 | 25 |
| Nitrites | mg/kg DW | 0.050 | 184 | 7.98 |
| Phosphorus | % DW | 0.050 | 0.124 | 0.105 |
| Phosphates | % DW | 0.10 | 0.28 | 0.24 |
| Sulphate | % DW | 0.10 | < 0.1 | < 0.1 |

Note: DW – dry weight

Ammonia shows a high concentration on the top section and about 1/4 of that on the bottom section. Nitrates and nitrites were also detected with the same behaviour – higher concentration on column top. When comparing both compounds to low concentrations detected in the outflow water it can be assumed that they were retained in the column. Also, by comparing nitrites to nitrates it's possible to see a higher concentration of nitrites on the top of the column and higher concentration of nitrates on the bottom. It can be assumed that the top section of Column 5 is more oxygenated than the bottom section, generating the degradation of ammonia on the top, then to nitrites and finally to nitrates at the bottom, where they were retained. While in Column 3 most ammonia was transformed into nitrites and nitrates that were leached in the outflow (not accumulating in the soils), Column 5 is a longer experiment (15 PV instead of 3 PV) leading to the accumulation of nitrites and nitrates in the top part of the soil column.

Again phosphorous and phosphates show lower concentrations in both sections when compared to Column 3, but in the same magnitude.

Similarly to Column 3 sulphates where not detected in bottom section, as well as on the top.

Concerning pharmaceuticals, the only value above LOR detected was in caffeine, in higher concentration on top section (57 mg/kg). Extended Column 5 soil analysis results are presented in Appendix 4.

### 4.3.2. Soil mixture

The results obtained in the experiments performed with natural soil (Section 4.3.1) showed the need to increase soil ability to retain some elements, namely pharmaceuticals, at the same time that the permeability, and therefore the infiltration rate, would be maintained or even increased. Based on these purposes, different mixtures of soils were defined and tested aiming to define the “perfect soil” for the future application in the SAT-MAR basins. These mixtures are composed of different proportions of: natural soil, organic soil, and sand (cf. Figure 19).

In the following sections the results concerning soil mixture characteristics (Section 4.3.2.1), hydraulic behaviour (Section 4.3.2.2) and quality aspects of outflow water (Section 4.3.2.3) are presented.

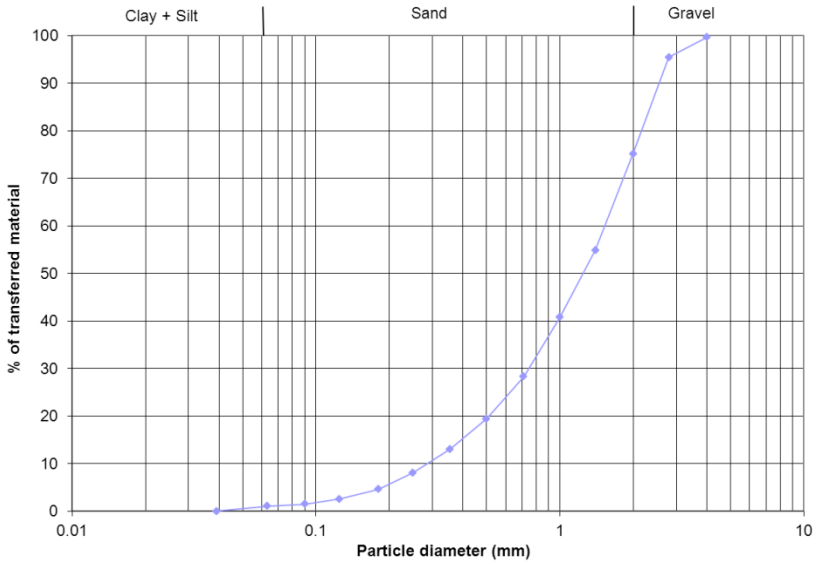
#### *4.3.2.1. Soil characteristics*

For natural soil component descriptions please refer to Section 4.3.1.1.

The carbonates percentage determined for the organic soil was 21%. Carbonates percentage was also determined for artificial sand. As expected 99% of this soil mixture component is carbonates, as it results from crushed limestone (see Section 4.2.2.4). The increase of carbonates may result in contaminant retaining processes.

Organic matter was not determined since the artificial sand is expected to have a null organic matter percentage due to its source (it’s not a soil itself) and the second component should have a organic matter percentage > 70% as stated by the seller.

A granulometric analysis for soil mixture was not possible due to the large organic content that would be severely altered by washing out and high temperature drying. For the same reason the organic soil was not submitted to this characterization. On the other hand, artificial sand was subjected to granulometric characterization – Graph 34




**Graph 34 – Artificial sand granulometric curve**

As expected, 98.1% of the particles are of the size of sands and 1.49% are below 0.063 mm.

Soil mixture bulk density and porosity where determined after column assembling and results are presented in Table 21.

**Table 21 – Soil mixture porosity and bulk density**

| | Column 6 | Column 7 | Column 8 | Column 9 |
|---|---|---|---|---|
| **Porosity (%)** | 45.0 | 53.1 | 74.8 | 69.8 |
| **Bulk density (g/cm$^3$)** | 1.09 | 0.93 | 1.23 | 1.19 |

Porosity values seem to be related to the percentage of artificial sand added to the soil mixture – Column 6 (60% natural, 40% organic) had the lower porosity value while Column 8 & Column 9 (40% natural, 20% organic, 40% artificial) had the higher porosity values. Column 7 presented the lower bulk density, although being similar to Column 6.

Both parameters are dependent not only in soil texture but also on the column packing. Since each soil mixture presented has its own characteristics, defining which factors will result in parameters variation is not possible. A larger set of soil mixtures with different percentages of components would be necessary to understand which effects they cause in soil characteristics and soil behaviour.

Although Column 8 and Column 9 have the same composition they show different porosity and bulk density. This may be related to column assembling factors and is discussed in Section 6.1.

#### *4.3.2.2. Soil hydraulic behaviour*

Soil-column experiments were conducted with different soil mixtures, namely to understand the short and long term effects in hydraulic behaviour. The results are summarized in Table 22.

**Table 22 – Soil mixture column experiments results for flow**

| | | Column 6 | Column 7 | Column 8 | Column 9 |
|---|---|---|---|---|---|
| **Experiment time length (days)** | | 4.0 | 4.0 | 46 | 46 |
| **Pore-volume (mL)** | | 265.2 | 312.4 | 440.2 | 411.1 |
| **Flow rate (cm$^3$/min)** | **Day 1** | 7.722 | 2.572 | 3.340 | 4.341 |
| | **Experiment time** | 4.931 | 1.789 | 0.792 | 1.272 |
| **Permeability (m/d)** | **Day 1** | 12.579 | 3.557 | 3.278 | 4.562 |
| | **Experiment time** | 8.032 | 2.474 | 0.777 | 1.337 |

Comparing pore-volume values, it noticeable that a decrease of the organic soil percentage and increase of artificial sand percentage in the mixture results in pore-volume increase. Again, as described previously, Column 8 and Column 9 show different pore-volumes, although the soil composition is exactly the same. These differences are also visible when comparing C8 and C9 flow rate and permeability. Both experiments were conducted with the

same type of inflow water matrix, thickness and assembling method, but C9 shows higher flow rates and permeability, which is almost the double that was verified in C8. Besides that factor, both C8 and C9 show lower permeability than C6 and C7, showing that the decrease of organic soil and increase of artificial results in a decrease of permeability.

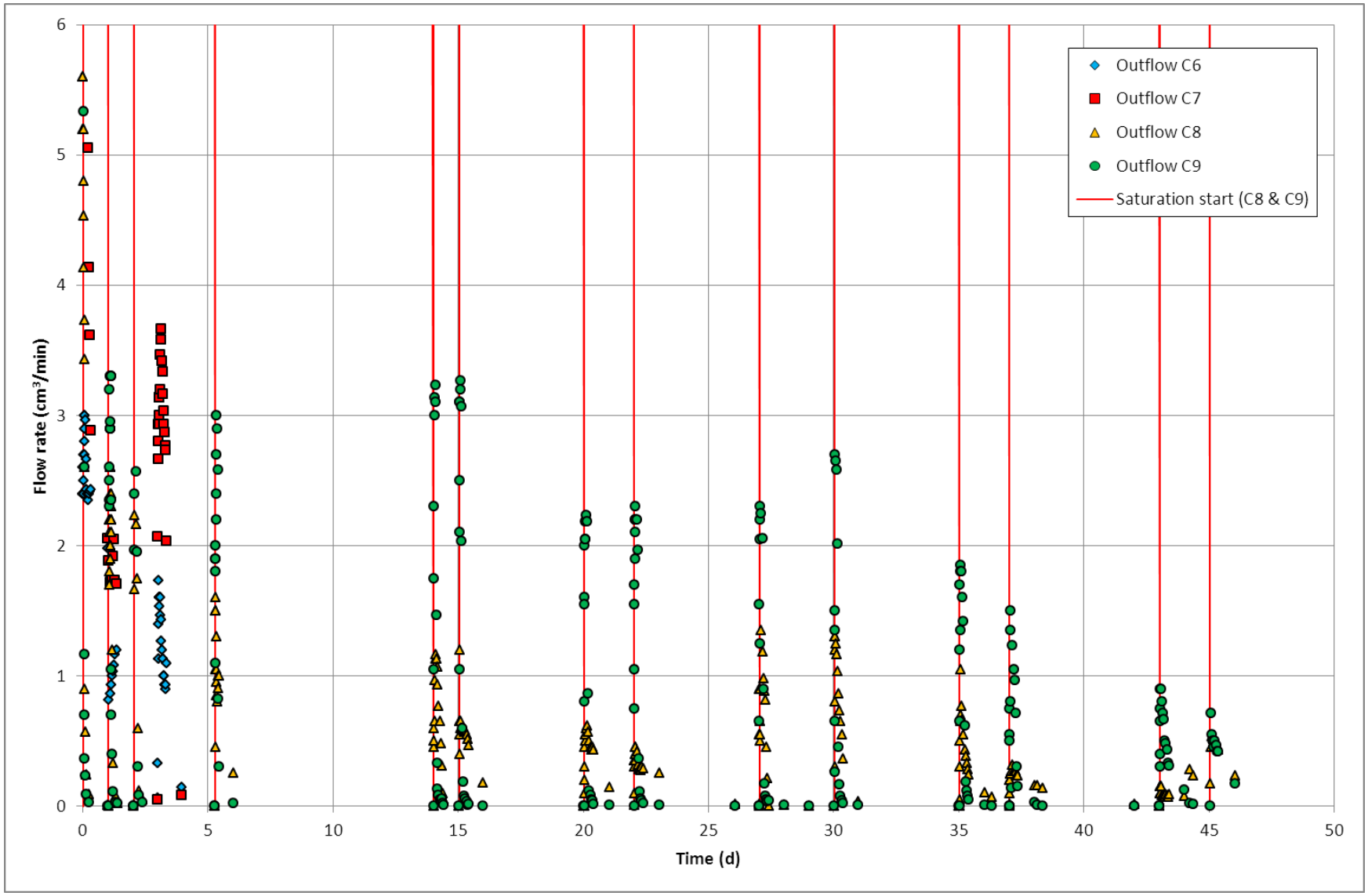
Both Graph 35 and Graph 36 show flow-rate changes throughout time and pore-volume respectively. For Column 6 and Column 7 a set of peaks were observed (easily observable in Flow rate vs Pore-volume graph) where there is an increase in flow rate and an abrupt change with a decrease of flow rate. Given that water injection was continuous and no alteration of injection flow was made, these peaks may result from soil washout and/or particle rearrangement that, after a period of decreasing permeability, result in lower flow rates with ponding above soil column. This hydraulic pressure resulting from ponding may have forced a preferential flow path (potentiated by soil wash out) and consequent particle rearrangement, therefore an increase in flow rates until stabilization.

Column 8 and Column 9 show fast response after each saturation period start and low ponding time as the flow rate rapidly increases. It's noticeable that C9 has almost double flow rates and consequently higher permeability, but shows very similar decrease times to C8 (approximately 1 day). Both columns show a smooth linear decrease of flow rates through time but a more steep decrease within the first pore-volume.

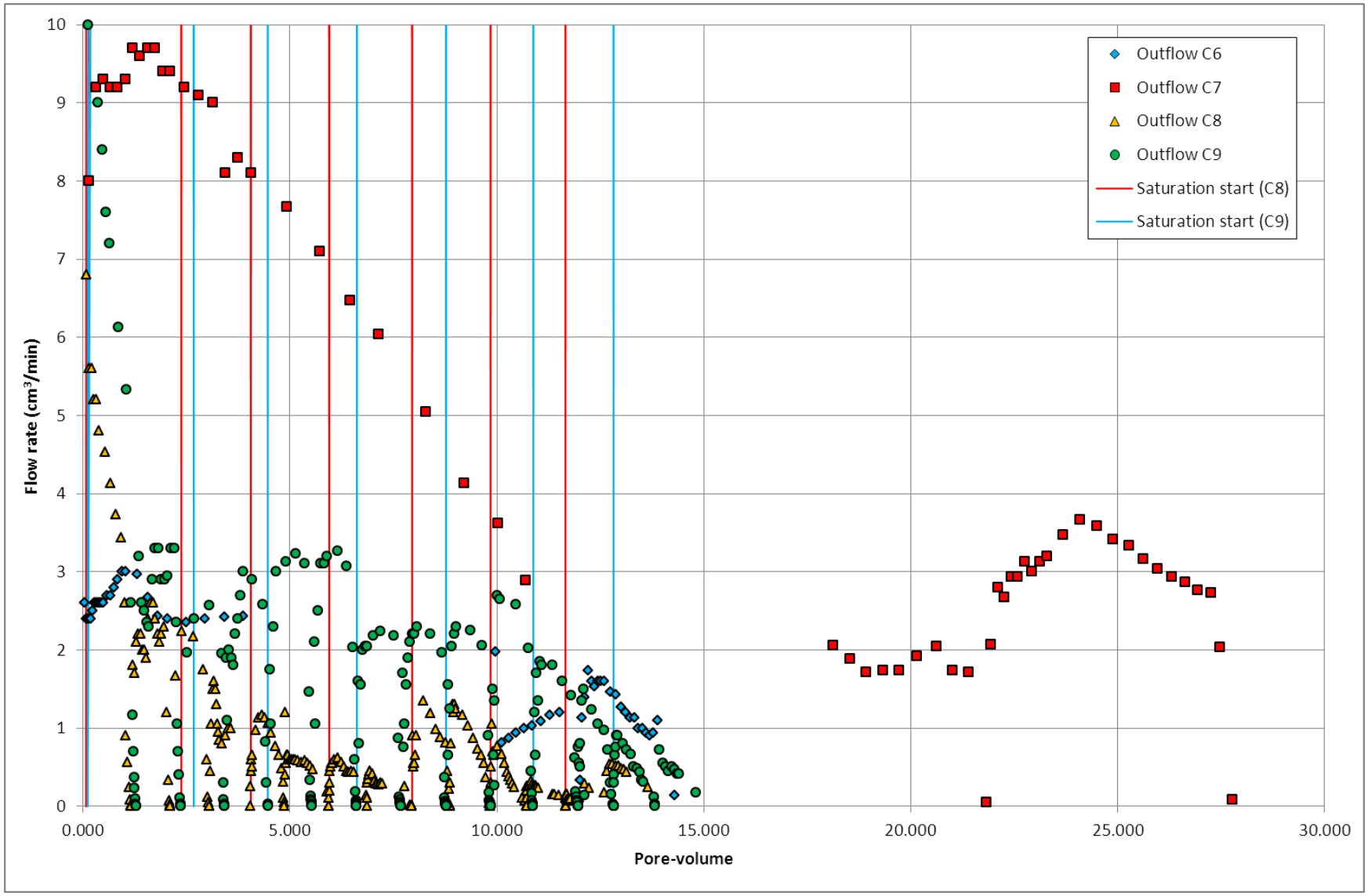
One of the facts that resulted in aborting soil-column experiment C6 and C7 was the continuous soil washout that created large macropores (and water/air pockets) - Figure 24. In Column 8 and Column 9 this washout processes was observed in the first 2 cycles, noticeable in the colour of the outflow water (which was slightly yellow), but no growing cavities were visible in the column walls.

**Figure 24 – Detail of soil washing out process (Column 6)**

Also, and possibly resulting from fine particle washout and rearrangement, a visible compaction process was observed in all columns but more noticeable in Column 6 and Column 7. While in Column 8 the maximum compaction observed was 1.5 cm, in Column 6 it achieved 3 cm. These processes showed a weak soil mixture structure and may have resulted in not good filtering layer as it was being continuously washed out.




**Graph 35 - Soil mixture hydraulic behaviour (time vs flow rate)**




**Graph 36 - Soil mixture hydraulic behaviour (time vs pore-volume)**

#### *4.3.2.3. Inflow/outflow results comparison*

The inflow and outflow samples collected in the soil-column experiments for the soil mixture are summarized in the following sections. Following the same procedure used for natural soil experiments, results were divided into subsections given the type of parameter considered – metals, nitrogen cycle components, major ions, and pharmaceuticals.

As stated previously, pharmaceuticals were only measured at Column 9 outflow, while the other parameters where determined for Column 8, assuming same conditions in the columns. Column 6 and 7 were only used for flow assessment, so no water or soil quality analysis was performed.

Outflow pH, Eh and electrical conductivity where measured in LASUB in both Column 8 and Column 9.

##### 4.3.2.3.1. Metals

Metals and metalloids concentrations in inflow and outflow water are presented in Graph 37 and Graph 38. Due to the differences in magnitude between the concentration values of phosphorous and manganese, they were presented in a separate graph.

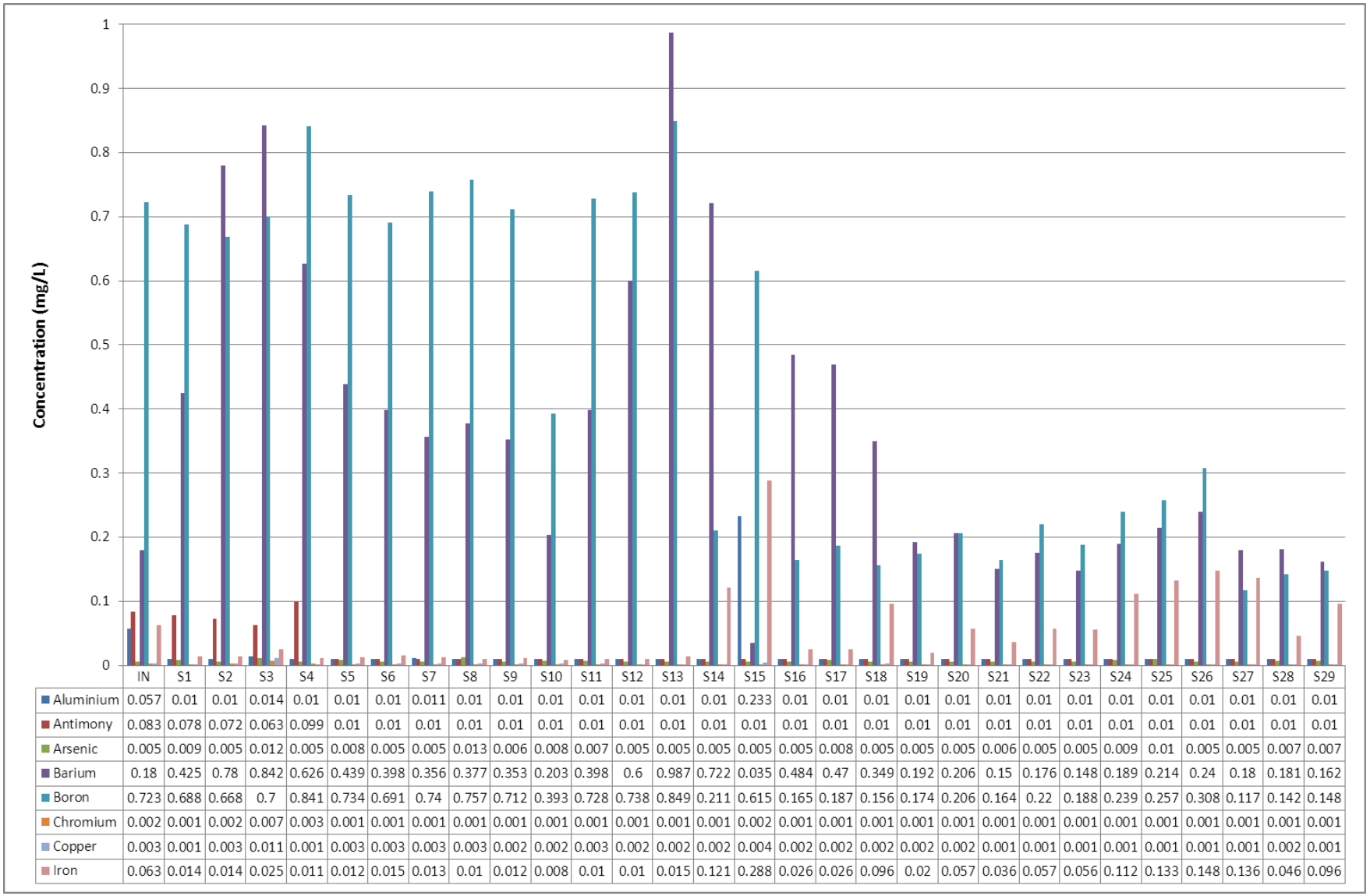
From the set of parameters presented in Graph 37, arsenic, chromium and copper show the lowest concentrations at inflow, while aluminium, antimony, iron, barium and boron show the highest values. Barium and boron show the highest concentrations of this set at outflow, and after outflow sample 13 (S13) there is a trend of decrease, with some oscillations.

Also after S13 iron concentration increases, and several samples after that show values above inflow concentration. This point may mark an alteration in the column conditions or the soil saturation in this element. At this point the pH values show a temporary decrease (between pore-volume 4 and 8 (cf. Graph 52), possibly responsible for the temporary release of some metals). S13 was the last sample to be collected before the experiment was stopped for one week. This longer unsaturation period, were injection stopped (and outflow flux was severely slowed as the soil mixture constituents, such as peat trend to have a great water retention capacity) may have resulted in a longer time of water soil interaction and better oxygenation. The potentiation of the reactions by the longer interaction may have resulted in lower pH in soil solution and processes of desorption processes in metals, that were ultimately mobilized when inflow was resumed one week later (and therefore higher concentrations in metals were measured).

Antimony show concentrations similar to inflow from sample S1 to S4 and then decreases and stabilizes its concentration along the experiment.

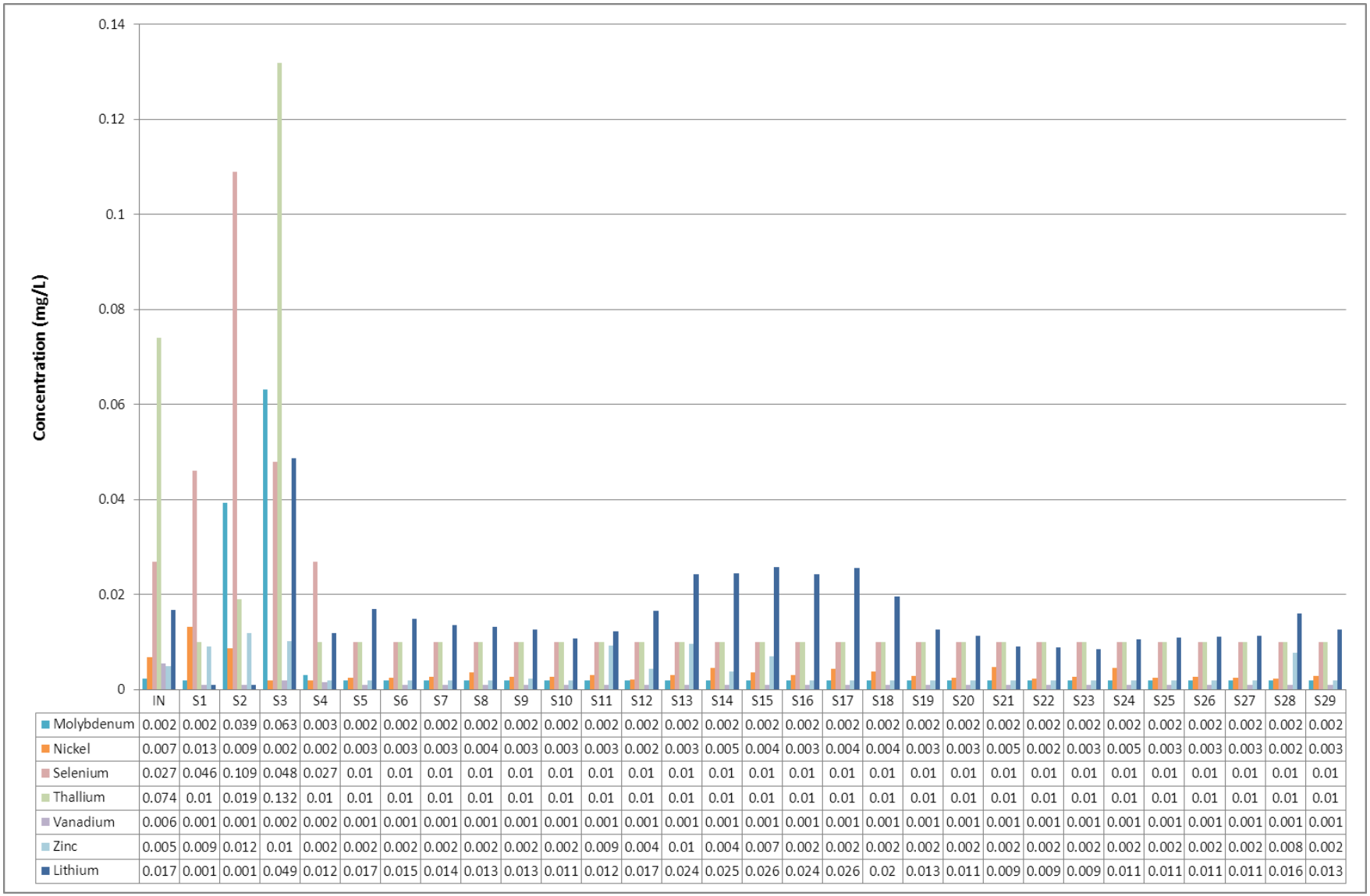
On the second set of metals (Graph 38), outflow samples show regular behaviour throughout the all experiment, having approximate inflow/outflow values, except for molybdenum, selenium, thallium and lithium. Those are higher in the first outflows, possibly as a result of the soil composition. The first metal has its concentration increasing between S2 and S3 suggesting a washout process, similarly to selenium and thallium. Lithium shows an increase of concentration between S2 and S18 and converges to values below inflow after that. The temporary increase of lithium between S13 and S18 possibly has the same reason, resulting from the pH decrease.

Finally, phosphorous shows at inflow relatively high concentrations, and assumes as oscillatory behaviour at outflow, with concentrations that can be approximately half of inflow. Manganese show also oscillatory behaviour with a possible washout process between S1 and S7 and S11 to S29 with concentrations always above inflow.



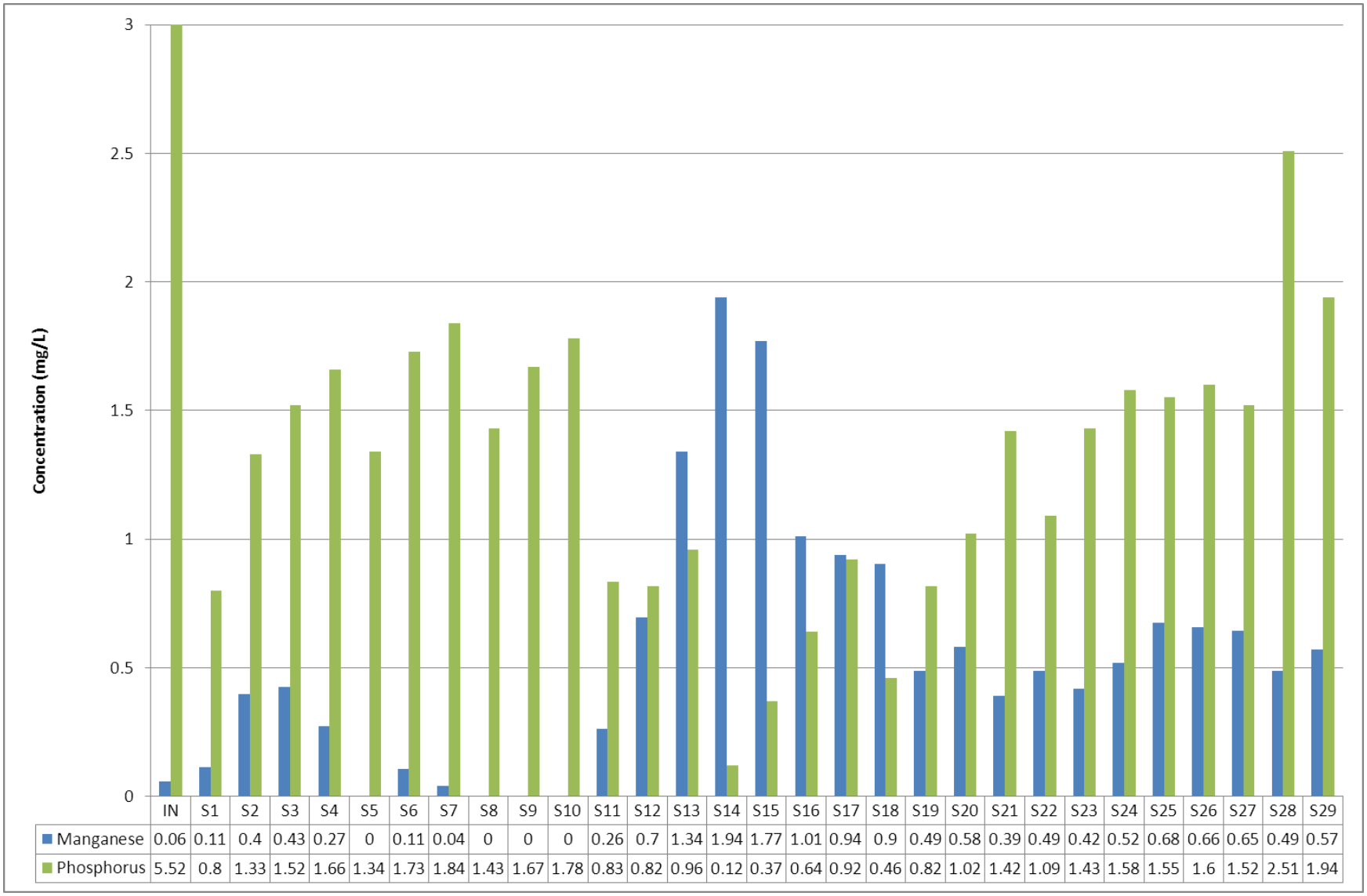

| | IN | S1 | S2 | S3 | S4 | S5 | S6 | S7 | S8 | S9 | S10 | S11 | S12 | S13 | S14 | S15 | S16 | S17 | S18 | S19 | S20 | S21 | S22 | S23 | S24 | S25 | S26 | S27 | S28 | S29 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Aluminium | 0.057 | 0.01 | 0.01 | 0.014 | 0.01 | 0.01 | 0.01 | 0.011 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.233 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Antimony | 0.083 | 0.078 | 0.072 | 0.063 | 0.099 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Arsenic | 0.005 | 0.009 | 0.005 | 0.012 | 0.005 | 0.008 | 0.005 | 0.005 | 0.013 | 0.006 | 0.008 | 0.007 | 0.005 | 0.005 | 0.005 | 0.005 | 0.005 | 0.008 | 0.005 | 0.005 | 0.005 | 0.006 | 0.005 | 0.005 | 0.009 | 0.01 | 0.005 | 0.005 | 0.007 | 0.007 |
| Barium | 0.18 | 0.425 | 0.78 | 0.842 | 0.626 | 0.439 | 0.398 | 0.356 | 0.377 | 0.353 | 0.203 | 0.398 | 0.6 | 0.987 | 0.722 | 0.035 | 0.484 | 0.47 | 0.349 | 0.192 | 0.206 | 0.15 | 0.176 | 0.148 | 0.189 | 0.214 | 0.24 | 0.18 | 0.181 | 0.162 |
| Boron | 0.723 | 0.688 | 0.668 | 0.7 | 0.841 | 0.734 | 0.691 | 0.74 | 0.757 | 0.712 | 0.393 | 0.728 | 0.738 | 0.849 | 0.211 | 0.615 | 0.165 | 0.187 | 0.156 | 0.174 | 0.206 | 0.164 | 0.22 | 0.188 | 0.239 | 0.257 | 0.308 | 0.117 | 0.142 | 0.148 |
| Chromium | 0.002 | 0.001 | 0.002 | 0.007 | 0.003 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.002 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 |
| Copper | 0.003 | 0.001 | 0.003 | 0.011 | 0.001 | 0.003 | 0.003 | 0.003 | 0.003 | 0.002 | 0.002 | 0.003 | 0.002 | 0.002 | 0.002 | 0.004 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.002 | 0.001 |
| Iron | 0.063 | 0.014 | 0.014 | 0.025 | 0.011 | 0.012 | 0.015 | 0.013 | 0.01 | 0.012 | 0.008 | 0.01 | 0.01 | 0.015 | 0.121 | 0.288 | 0.026 | 0.026 | 0.096 | 0.02 | 0.057 | 0.036 | 0.057 | 0.056 | 0.112 | 0.133 | 0.148 | 0.136 | 0.046 | 0.096 |

**Graph 37 – Metals inflow/outflow concentration in Column 8 (1st set)**




| | IN | S1 | S2 | S3 | S4 | S5 | S6 | S7 | S8 | S9 | S10 | S11 | S12 | S13 | S14 | S15 | S16 | S17 | S18 | S19 | S20 | S21 | S22 | S23 | S24 | S25 | S26 | S27 | S28 | S29 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Molybdenum | 0.002 | 0.002 | 0.039 | 0.063 | 0.003 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 |
| Nickel | 0.007 | 0.013 | 0.009 | 0.002 | 0.002 | 0.003 | 0.003 | 0.003 | 0.004 | 0.003 | 0.003 | 0.003 | 0.002 | 0.003 | 0.005 | 0.004 | 0.003 | 0.004 | 0.004 | 0.003 | 0.003 | 0.005 | 0.002 | 0.003 | 0.005 | 0.003 | 0.003 | 0.003 | 0.002 | 0.003 |
| Selenium | 0.027 | 0.046 | 0.109 | 0.048 | 0.027 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Thallium | 0.074 | 0.01 | 0.019 | 0.132 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Vanadium | 0.006 | 0.001 | 0.001 | 0.002 | 0.002 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 |
| Zinc | 0.005 | 0.009 | 0.012 | 0.01 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.009 | 0.004 | 0.01 | 0.004 | 0.007 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.008 | 0.002 |
| Lithium | 0.017 | 0.001 | 0.001 | 0.049 | 0.012 | 0.017 | 0.015 | 0.014 | 0.013 | 0.013 | 0.011 | 0.012 | 0.017 | 0.024 | 0.025 | 0.026 | 0.024 | 0.026 | 0.02 | 0.013 | 0.011 | 0.009 | 0.009 | 0.009 | 0.011 | 0.011 | 0.011 | 0.011 | 0.016 | 0.013 |

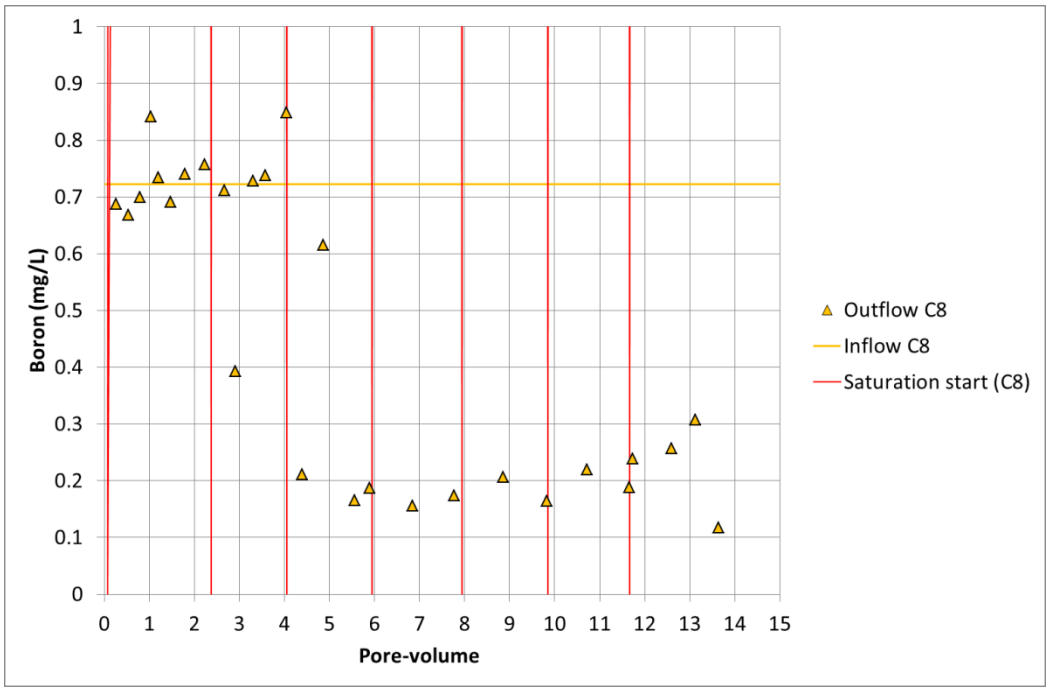
**Graph 38 – Metals inflow/outflow concentration in Column 8 (2nd set)**




| | IN | S1 | S2 | S3 | S4 | S5 | S6 | S7 | S8 | S9 | S10 | S11 | S12 | S13 | S14 | S15 | S16 | S17 | S18 | S19 | S20 | S21 | S22 | S23 | S24 | S25 | S26 | S27 | S28 | S29 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Manganese | 0.06 | 0.11 | 0.4 | 0.43 | 0.27 | 0 | 0.11 | 0.04 | 0 | 0 | 0 | 0.26 | 0.7 | 1.34 | 1.94 | 1.77 | 1.01 | 0.94 | 0.9 | 0.49 | 0.58 | 0.39 | 0.49 | 0.42 | 0.52 | 0.68 | 0.66 | 0.65 | 0.49 | 0.57 |
| Phosphorus | 5.52 | 0.8 | 1.33 | 1.52 | 1.66 | 1.34 | 1.73 | 1.84 | 1.43 | 1.67 | 1.78 | 0.83 | 0.82 | 0.96 | 0.12 | 0.37 | 0.64 | 0.92 | 0.46 | 0.82 | 1.02 | 1.42 | 1.09 | 1.43 | 1.58 | 1.55 | 1.6 | 1.52 | 2.51 | 1.94 |

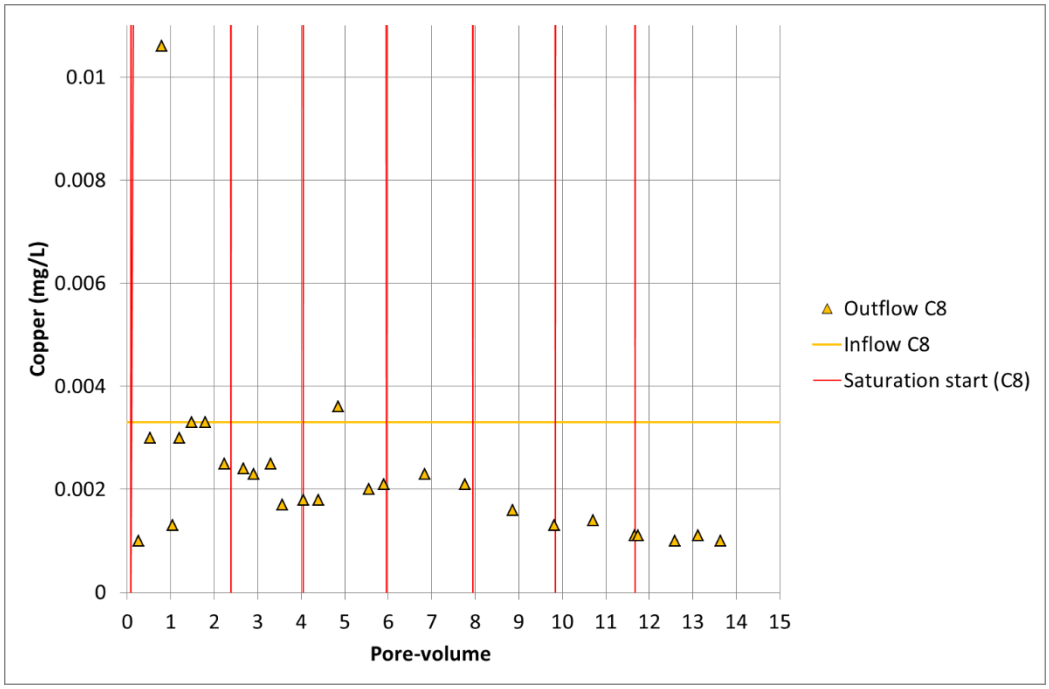
**Graph 39 – Manganese and phosphorus inflow/outflow concentration in Column 8**

Analysing in detail some of the metals, Graph 40, Graph 41 and Graph 42 present boron, copper and zinc concentrations at the outflow.



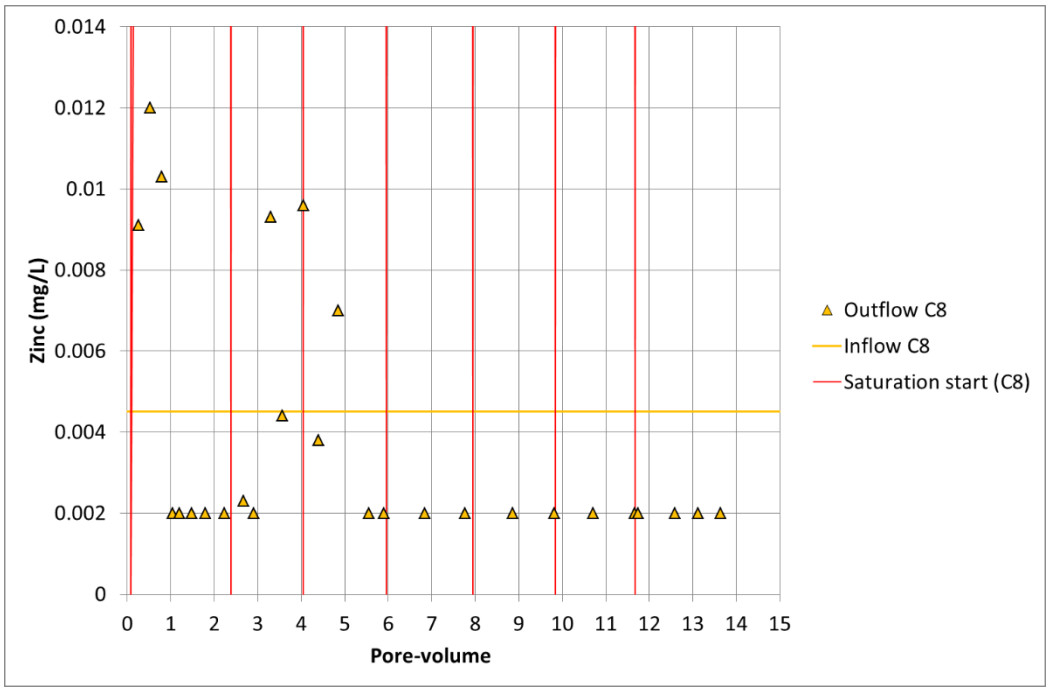

**Graph 40 – Boron vs pore-volume (soil mixture)**

Boron shows its conservative behaviour between experiment start and PV3-PV4. After that boron concentrations measured are always below inflow concentration with a tenuous increase trend from PV10. Assuming that the inflow concentration remains the same it can be assumed that a retention mechanism is causing a smaller concentration in outflow. Even though B is an anion, which is likely to be conservative as $Cl^-$ or $NO_3^-$, B is sorbed more strongly by soils than other anions and the manner of its sorption by clay surface or organic matter is somewhat similar to that of cations, for example as $B(OH)_4^-$. Being this soil mixture more rich in organic matter, the better performance in B behaviour is due to that.




**Graph 41 – Copper vs pore-volume (soil mixture)**

A copper washing out process seems to occur between experiment start and PV1, and after that the concentration at outflow show a decreasing trend. The only exception is at PV5. These results are similar to those obtained in the natural soil-column experiments.




**Graph 42 - Zinc vs pore-volume (soil mixture)**

Zinc only show above LOR outflow concentration between experiment start and PV1 – which again seems evidence of soil washout – and between PV3 and P5. Again the behaviour is very similar to that obtained in natural soil experiments, which ability to retain this metal and

Cu was already good. Also the increase of OM in soil percentage could have helped in the retention of this metal as this component is an important factor affecting behaviour of Zn in soil, which results in higher adsorption capabilities (Alloway, 1990).

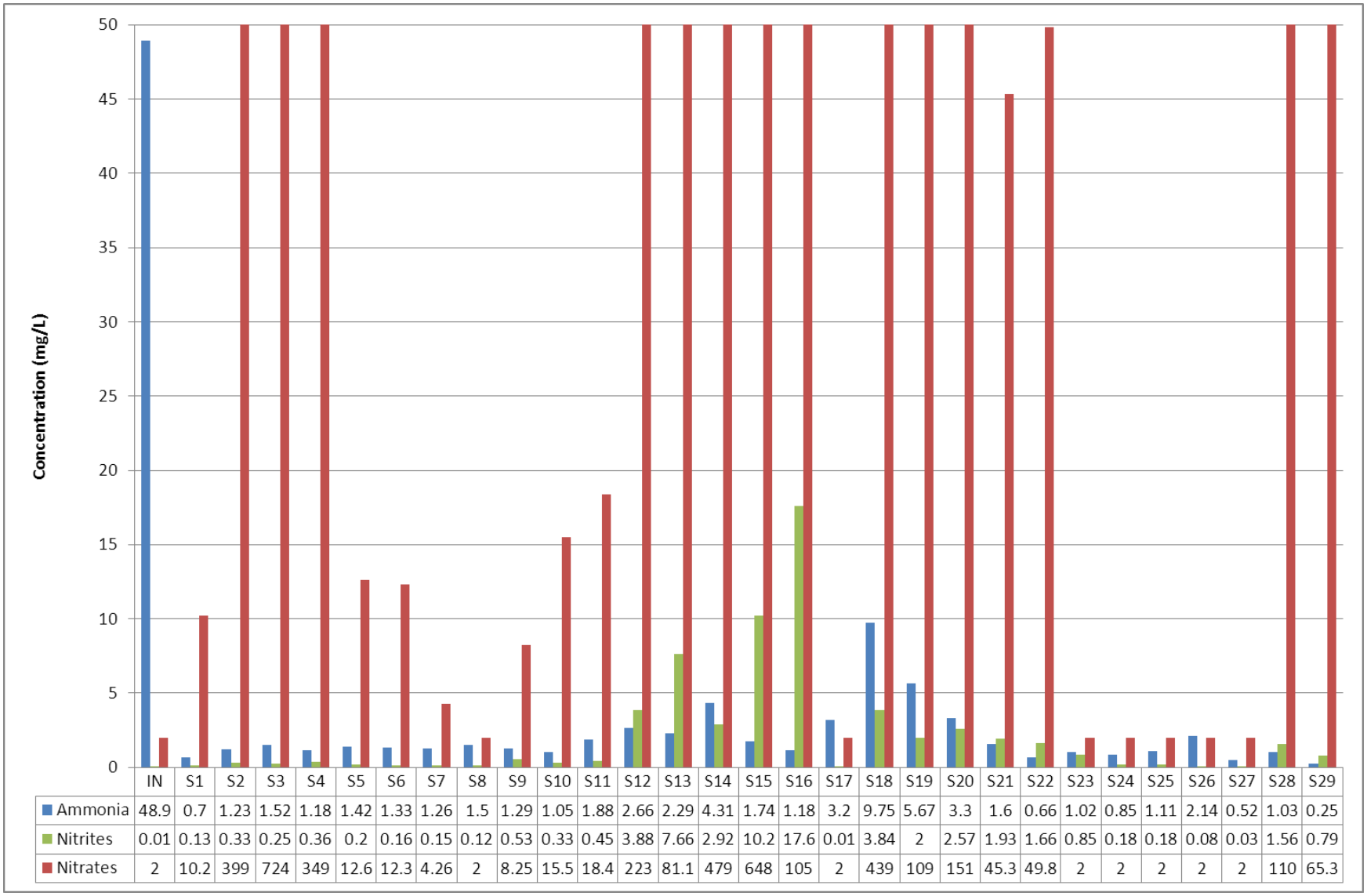
#### 4.3.2.3.2. Nitrogen cycle

Concerning the nitrogen cycle Graph 43 summarizes the inflow/outflow results for Column 8.

Inflow water present high concentration in ammonia while nitrites and nitrates concentration are bellow LOR.

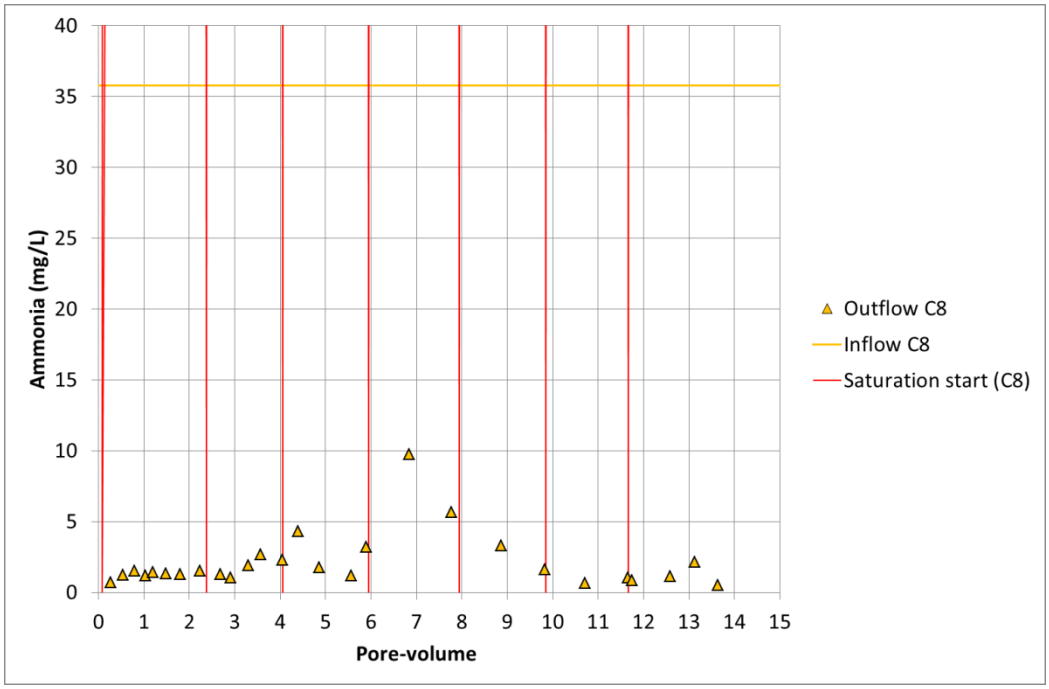
At the outflow, ammonia decreases in concentration, compared with inflow, while nitrites reappears between S12 and S23. Nitrates show very high values, several orders of magnitude compared to inflow. The maximum value measured is 724 mg/L at outflow sample 3. This high concentration may be directly related to the soil mixtures organic component. Considering that it represents a commercial soil, nitrogen may have been added to its composition, being slowly released during the experiment. Again the changes observed during S13 and S18 may have created conditions that prevented the oxidation of nitrites to nitrates.

Ammonia, nitrites and nitrates concentration along pore-volume are presented in Graph 44, Graph 45 and Graph 46.



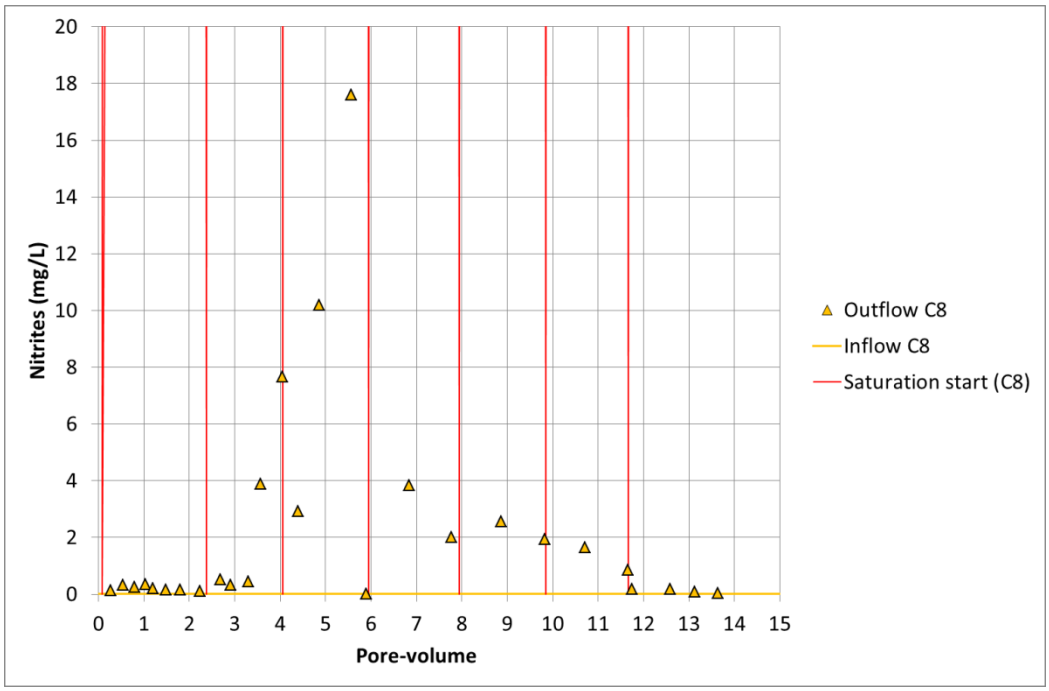

| | IN | S1 | S2 | S3 | S4 | S5 | S6 | S7 | S8 | S9 | S10 | S11 | S12 | S13 | S14 | S15 | S16 | S17 | S18 | S19 | S20 | S21 | S22 | S23 | S24 | S25 | S26 | S27 | S28 | S29 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ammonia | 48.9 | 0.7 | 1.23 | 1.52 | 1.18 | 1.42 | 1.33 | 1.26 | 1.5 | 1.29 | 1.05 | 1.88 | 2.66 | 2.29 | 4.31 | 1.74 | 1.18 | 3.2 | 9.75 | 5.67 | 3.3 | 1.6 | 0.66 | 1.02 | 0.85 | 1.11 | 2.14 | 0.52 | 1.03 | 0.25 |
| Nitrites | 0.01 | 0.13 | 0.33 | 0.25 | 0.36 | 0.2 | 0.16 | 0.15 | 0.12 | 0.53 | 0.33 | 0.45 | 3.88 | 7.66 | 2.92 | 10.2 | 17.6 | 0.01 | 3.84 | 2 | 2.57 | 1.93 | 1.66 | 0.85 | 0.18 | 0.18 | 0.08 | 0.03 | 1.56 | 0.79 |
| Nitrates | 2 | 10.2 | 399 | 724 | 349 | 12.6 | 12.3 | 4.26 | 2 | 8.25 | 15.5 | 18.4 | 223 | 81.1 | 479 | 648 | 105 | 2 | 439 | 109 | 151 | 45.3 | 49.8 | 2 | 2 | 2 | 2 | 2 | 110 | 65.3 |

**Graph 43 - Nitrogen cycle components concentration in Column 8 inflow/outflow**




**Graph 44 - Ammonia vs pore-volume (soil mixture)**

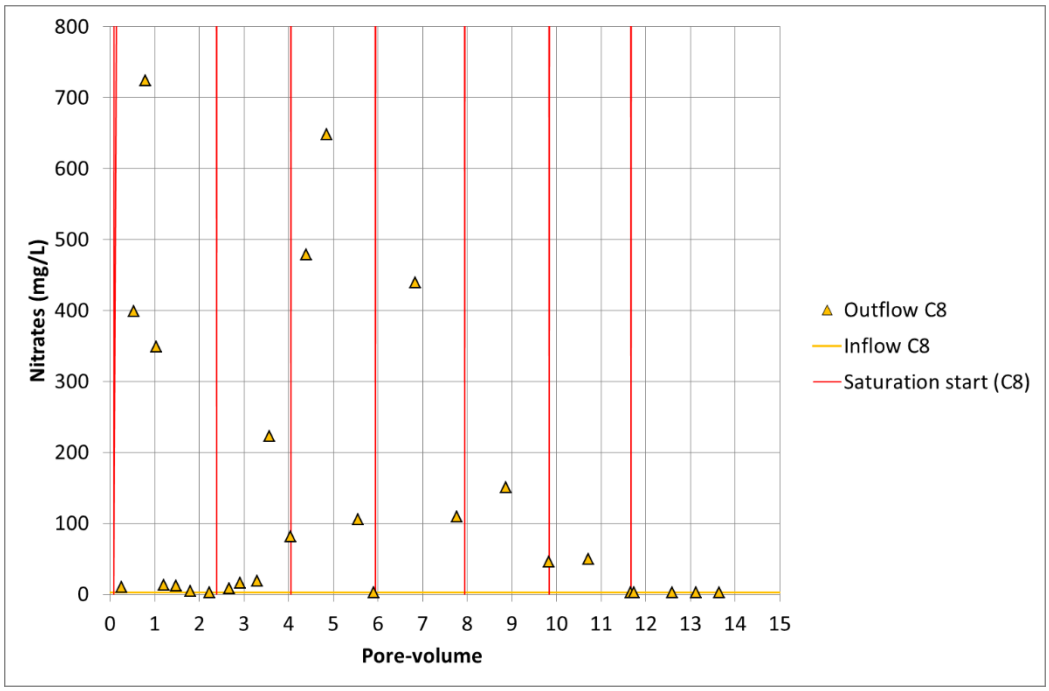
Ammonia outflow values are, as previously stated, always below inflow concentration, with only a slight increase between PV4-PV8. This also represents that in several periods the column is being oxygenated and ammonia is being degraded into nitrites and nitrates.




**Graph 45 - Nitrites vs pore-volume (soil mixture)**

Nitrites also show an increase in concentration between PV4 and PV7, that remained until PV11. Comparing with ammonia this may represent a period when the conditions inside the column have changed, allowing for the nitrogen cycle to invert resulting in transformation of

nitrites and ammonia, by low oxygen levels inside it. Values are always above inflow concentrations.




**Graph 46 - Nitrates vs pore-volume (soil mixture)**

As presented above nitrates detected in outflow can achieve high values in several hundreds of mg/L. That nitrites concentration seems regular between PV1-PV3 and also between PV12-PV14.

Such high concentration of nitrates due to possible soil and organic matter washout end up disguising the nitrogen cycle processes inside the column, not allowing to compare nitrates outflow concentration with nitrites and ammonia with such different orders of magnitude.

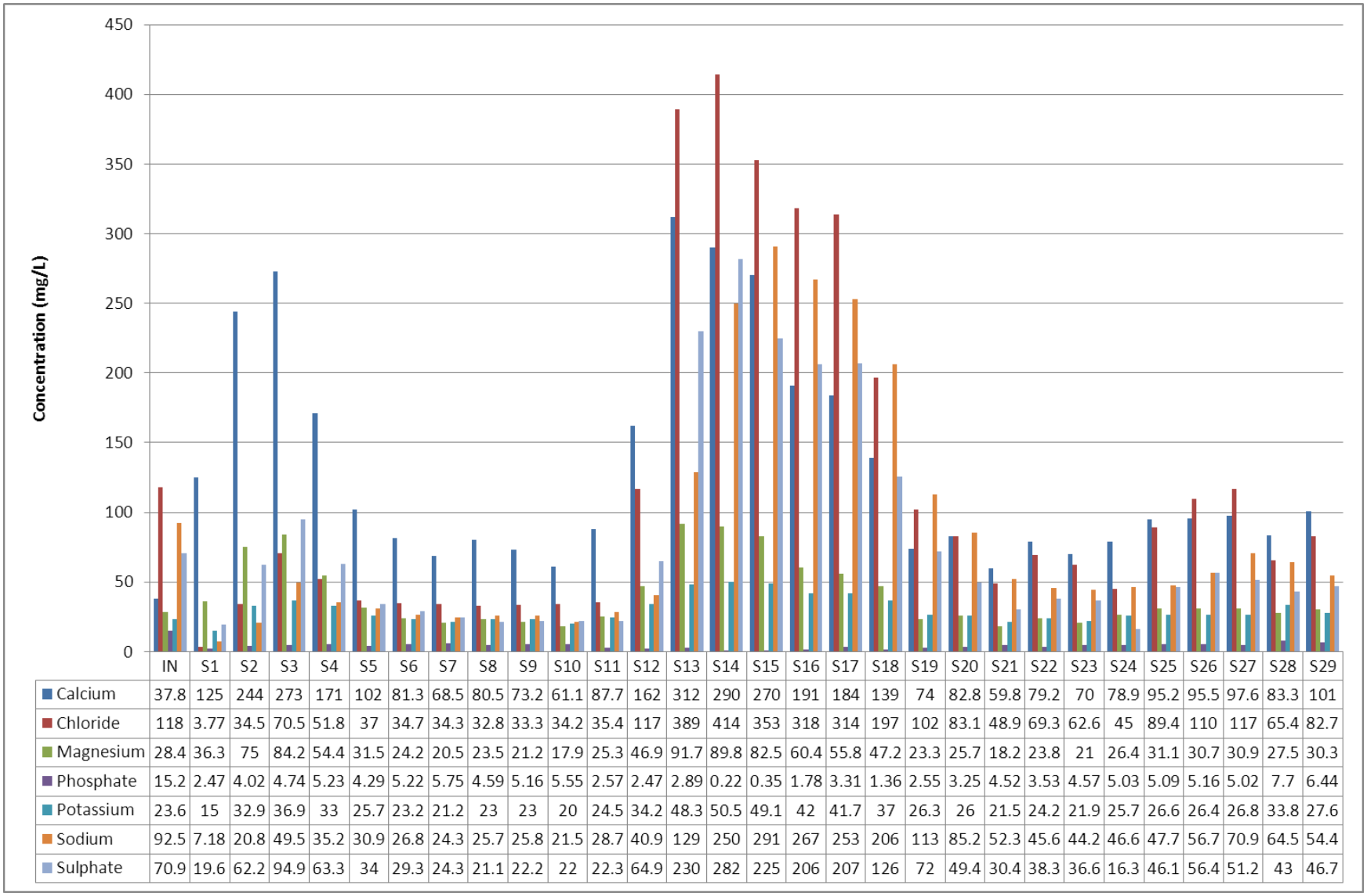
The presence of the organic soil does not favour the outflow concentrations of nitrates and nitrites, but in the real scale SAT-MAR basin it is expected that nitrate reduction can occur in reducing environment producing $N_2$ gas, that will escape to the atmosphere:

$$2\ NO_3^- + 12\ H^+ + 10\ e^- \rightarrow N_2\ (g) + 6\ H_2O$$

#### 4.3.2.3.3. Major ions

Calcium, chloride, magnesium, phosphate, potassium, sodium and sulphate concentration results are presented in Graph 47.

Again bicarbonate concentrations were not measured as the necessary volume was too high.




| | IN | S1 | S2 | S3 | S4 | S5 | S6 | S7 | S8 | S9 | S10 | S11 | S12 | S13 | S14 | S15 | S16 | S17 | S18 | S19 | S20 | S21 | S22 | S23 | S24 | S25 | S26 | S27 | S28 | S29 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Calcium | 37.8 | 125 | 244 | 273 | 171 | 102 | 81.3 | 68.5 | 80.5 | 73.2 | 61.1 | 87.7 | 162 | 312 | 290 | 270 | 191 | 184 | 139 | 74 | 82.8 | 59.8 | 79.2 | 70 | 78.9 | 95.2 | 95.5 | 97.6 | 83.3 | 101 |
| Chloride | 118 | 3.77 | 34.5 | 70.5 | 51.8 | 37 | 34.7 | 34.3 | 32.8 | 33.3 | 34.2 | 35.4 | 117 | 389 | 414 | 353 | 318 | 314 | 197 | 102 | 83.1 | 48.9 | 69.3 | 62.6 | 45 | 89.4 | 110 | 117 | 65.4 | 82.7 |
| Magnesium | 28.4 | 36.3 | 75 | 84.2 | 54.4 | 31.5 | 24.2 | 20.5 | 23.5 | 21.2 | 17.9 | 25.3 | 46.9 | 91.7 | 89.8 | 82.5 | 60.4 | 55.8 | 47.2 | 23.3 | 25.7 | 18.2 | 23.8 | 21 | 26.4 | 31.1 | 30.7 | 30.9 | 27.5 | 30.3 |
| Phosphate | 15.2 | 2.47 | 4.02 | 4.74 | 5.23 | 4.29 | 5.22 | 5.75 | 4.59 | 5.16 | 5.55 | 2.57 | 2.47 | 2.89 | 0.22 | 0.35 | 1.78 | 3.31 | 1.36 | 2.55 | 3.25 | 4.52 | 3.53 | 4.57 | 5.03 | 5.09 | 5.16 | 5.02 | 7.7 | 6.44 |
| Potassium | 23.6 | 15 | 32.9 | 36.9 | 33 | 25.7 | 23.2 | 21.2 | 23 | 23 | 20 | 24.5 | 34.2 | 48.3 | 50.5 | 49.1 | 42 | 41.7 | 37 | 26.3 | 26 | 21.5 | 24.2 | 21.9 | 25.7 | 26.6 | 26.4 | 26.8 | 33.8 | 27.6 |
| Sodium | 92.5 | 7.18 | 20.8 | 49.5 | 35.2 | 30.9 | 26.8 | 24.3 | 25.7 | 25.8 | 21.5 | 28.7 | 40.9 | 129 | 250 | 291 | 267 | 253 | 206 | 113 | 85.2 | 52.3 | 45.6 | 44.2 | 46.6 | 47.7 | 56.7 | 70.9 | 64.5 | 54.4 |
| Sulphate | 70.9 | 19.6 | 62.2 | 94.9 | 63.3 | 34 | 29.3 | 24.3 | 21.1 | 22.2 | 22 | 22.3 | 64.9 | 230 | 282 | 225 | 206 | 207 | 126 | 72 | 49.4 | 30.4 | 38.3 | 36.6 | 16.3 | 46.1 | 56.4 | 51.2 | 43 | 46.7 |

**Graph 47 – Column 8 major ions inflow/outflow concentrations**

When comparing calcium and magnesium inflow and outflow concentrations, it's again possible to observe a continuous soil washing out processe, where high concentrations along all samples are detected, except for magnesium that tends to stabilize between S6 and S11 and S19 and S29. Given that limestone is added to the soil mixture these outflow concentrations in calcium and magnesium were expected.

Sodium and sulphate have also higher concentrations at inflow. Both show great increase between S12 and S20. Comparing with other parameters previously presented for this column, there seems to be a generalized increase of concentrations between S12 and S20. Chloride also follows this behaviour. Again almost all of these samples, mainly after S13, were collected after a long period of desaturation, where the experiment was stopped for 1 week. This may have allowed for the good oxygenation of the soil, as well as a change in the column conditions, as the sat/unsaturation interval greatly increased when compared with the others.

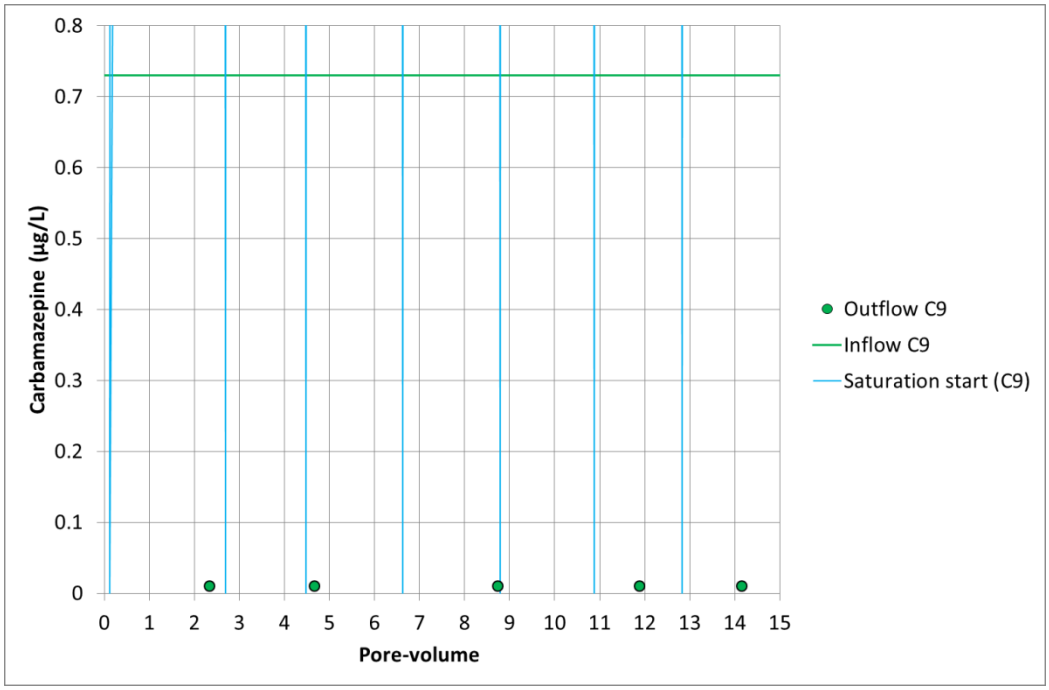
This may have also resulted from inflow sample composition variation, but this will be further discussed in Section 6.1.

#### 4.3.2.3.4. Pharmaceuticals

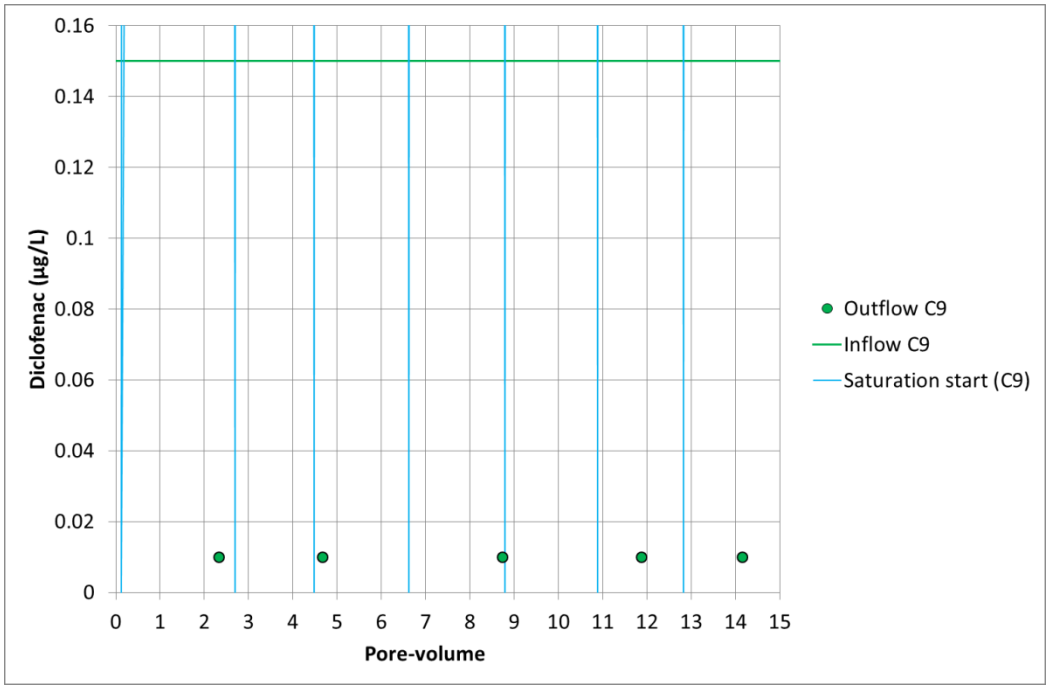
A set of 24 pharmaceuticals were analysed at the 4 samples collected at Column 9 outflow.

In the inflow water, as presented in Table 13 (Section 4.2.3), 9 out of 24 pharmaceuticals showed concentrations above LOR – atenolol, bisoprolol, metoprolol, propranolol, sotalol, diclofenac, gemfibrozil, naproxen and carbamazepine.

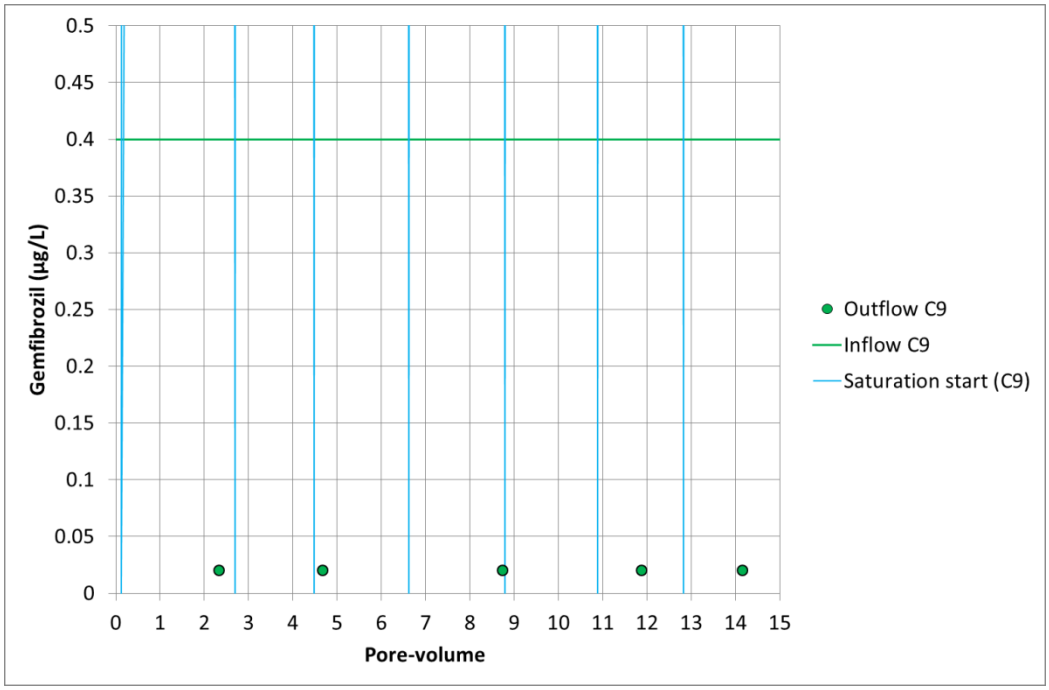
Following the methodology presented in Section 4.3.1.3.4, graphics for carbamazepine, diclofenac, gemfibrozil and naproxen are presented in Graph 48, Graph 49, Graph 50 and Graph 51.



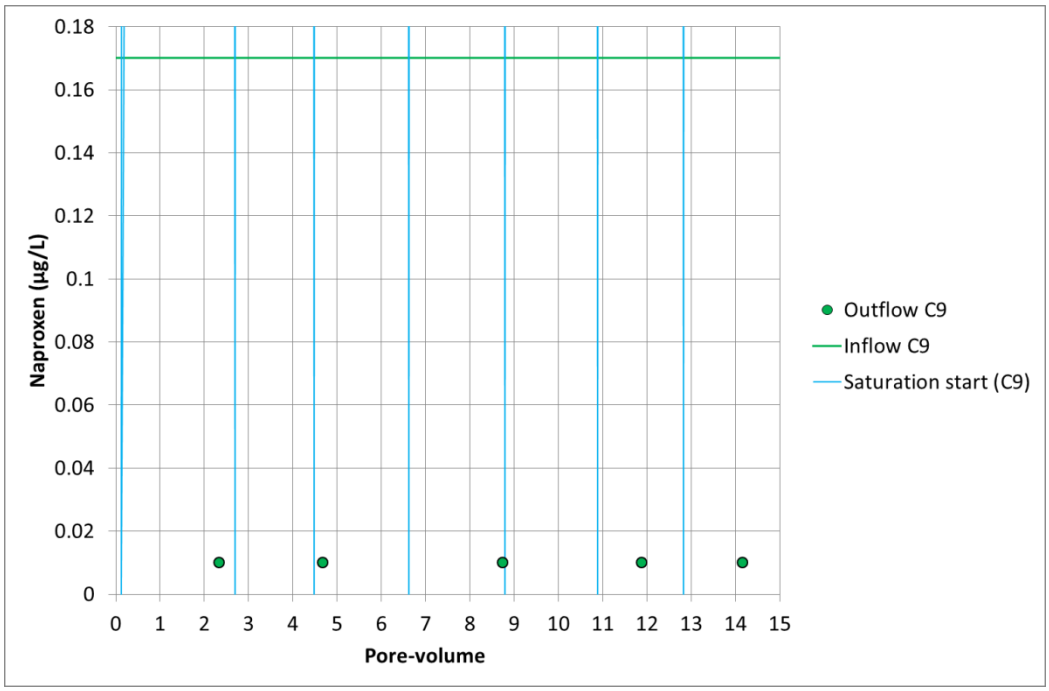

**Graph 48 – Carbamazepine vs pore-volume (soil mixture)**




**Graph 49 – Diclofenac vs pore-volume (soil mixture)**




**Graph 50 – Gemfibrozil vs pore-volume (soil mixture)**



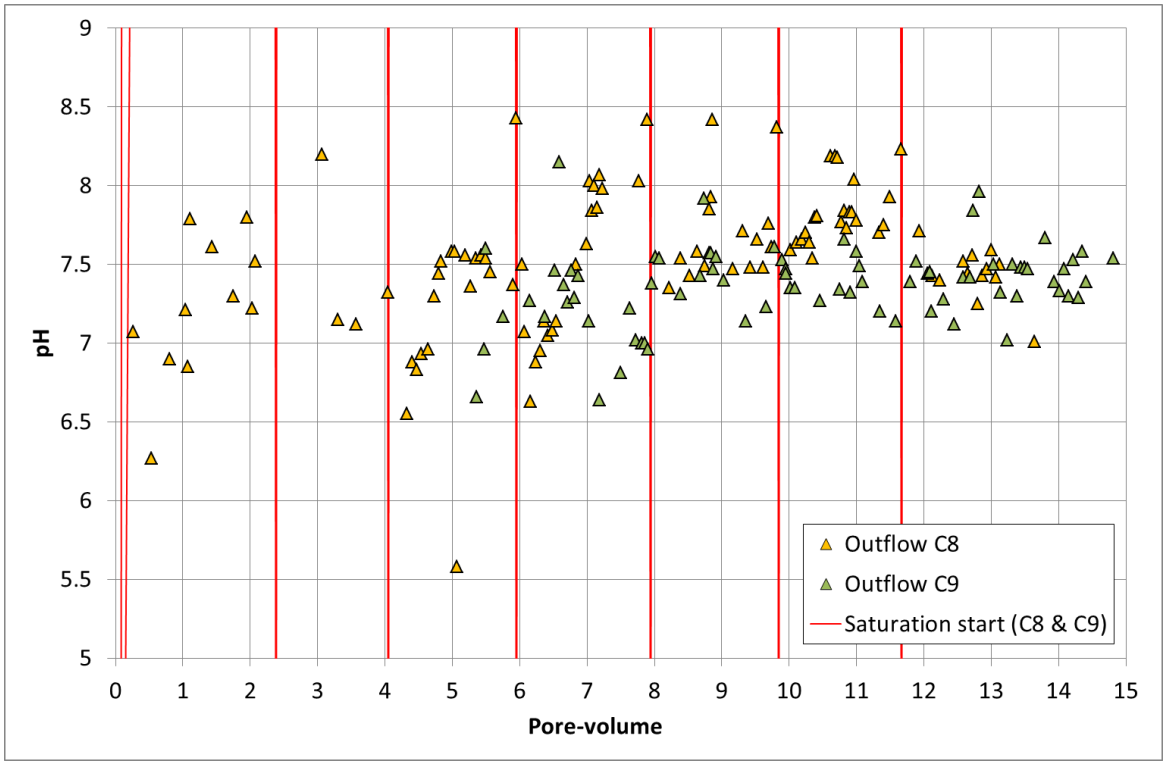

**Graph 51 – Naproxen vs pore-volume (soil mixture)**

Comparing with inflow data, and considering that inflow concentrations remain the same throughout the experiment, it's possible to observe that none of the pharmaceuticals were detected at outflow – concentrations are below LOR. This may have been a result of soil retention and/or biodegradation.

#### 4.3.2.3.5. pH, Eh and electrical conductivity

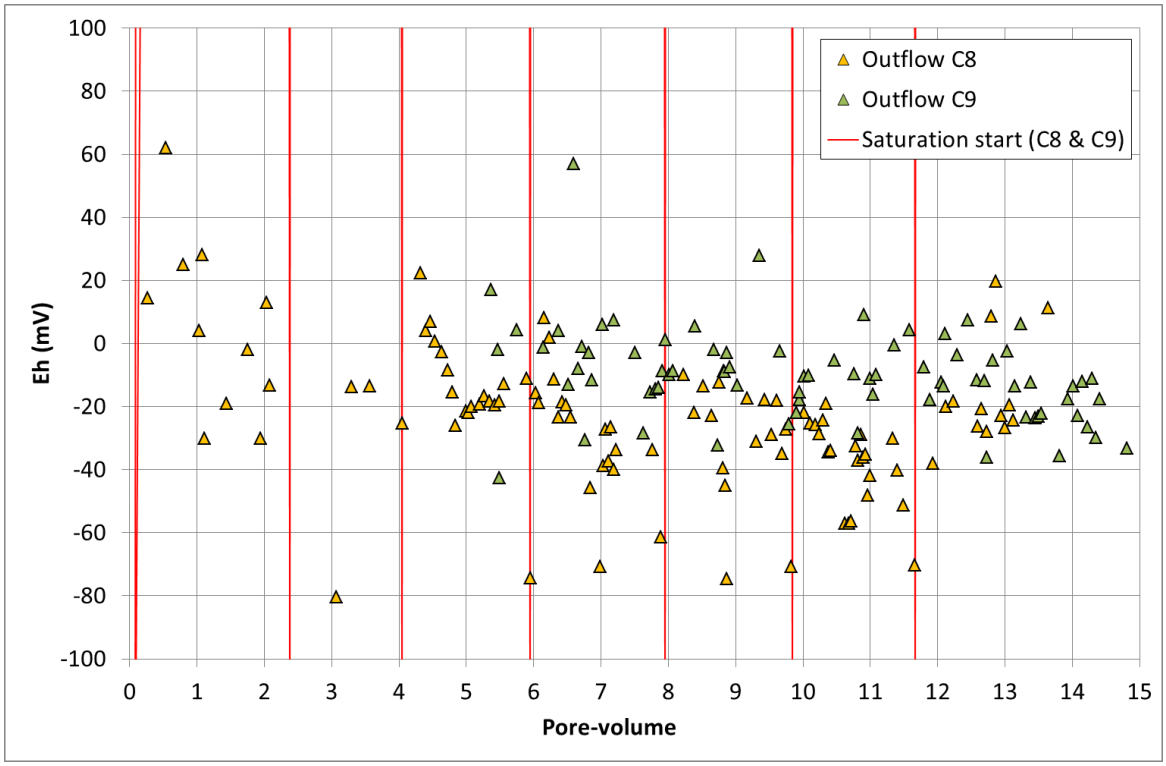
Similarly to natural soil-column experiments, pH, redox potential (Eh) and electrical conductivity were measured once the necessary volume at outflow was achieved. Results for these three parameters, in terms of pore-volumes, are presented in Graph 52 to Graph 54.

Column 8 and Column 9 show similar behaviour with pH situated between 6 and 8.5, with the exception of sample collected at PV5 where pH is approximately 5.5 (with no noticeable changes in the condition of the experiment during that period this may be an error of measurement). No specific trend is observable and values are not very far from the inflow water pH (7.28). This means that no significant alteration is occurring in the solution pH inside the column along the experiments, except for the period between PV4 and PV8, which is the only one with pH < 7 after the experiment started (post PV1). That particular change has had important consequences in some metals remobilization, with clear increase in their concentration in the outflow water for that period.

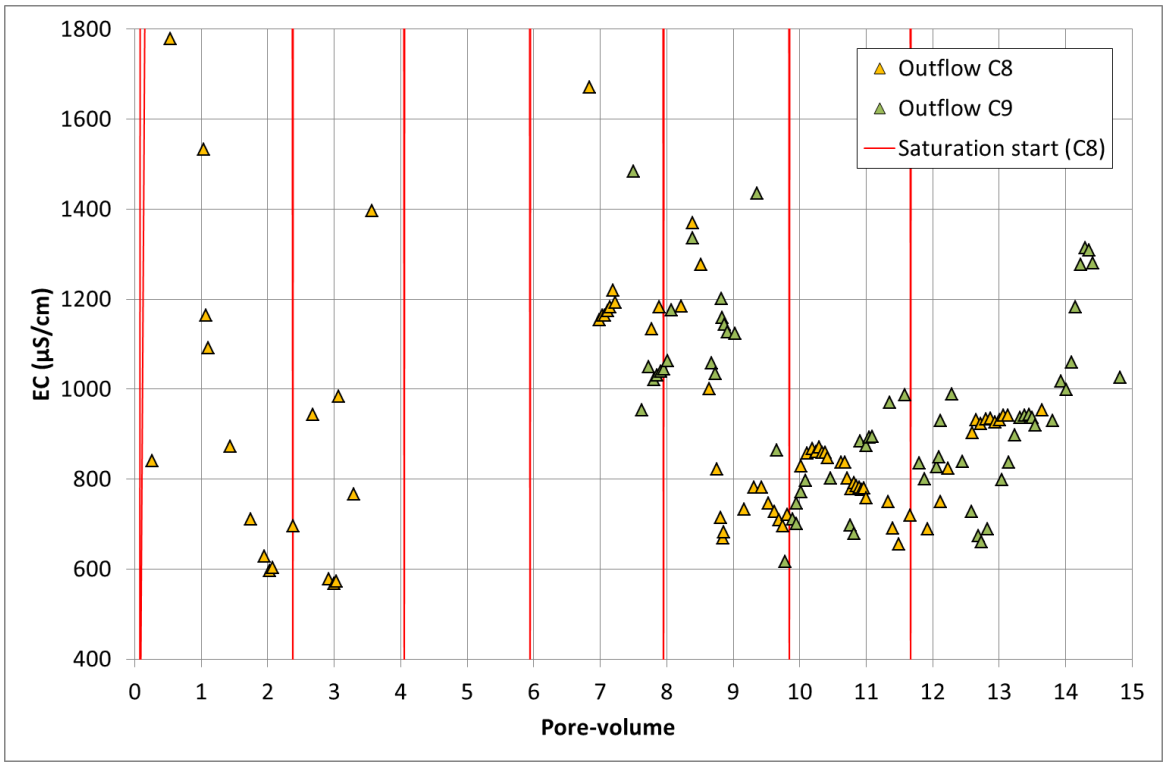



**Graph 52 – pH vs pore-volume (soil mixture)**

Concerning Eh parameter, a similar behaviour is observed between C8 and C9, with Eh at outflow lower than inflow (90 mV). Again no specific trend is clear, and a low oxygenated environment is observed.




**Graph 53 – Redox potential vs pore-volume (soil mixture)**




**Graph 54 – Electrical conductivity vs pore-volume (soil mixture)**

Electrical conductivity doesn't show a clear trend in both columns considering inflow value (1052 µS/cm), although from PV9-10 values are below inflow. In column 8 this parameter increases significantly between experiment start and PV1 and decreases again until PV2. This suggests that deionized water/wastewater mixture occurs rapidly and a soil washout process starts (as electrical conductivity values increase until approximately 1800 µS/cm, higher than inflow). After a new saturation cycle there is a new increase but not as clear as the previous. Column 9 show no obvious behaviour with an increase in electrical conductivity in all experiment time, but after PV12-13 appears to be a clear increasing and continuous trend.

## 4.4. Batch experiments

Two batch experiments were conducted to understand, in equilibrium conditions, what is the behaviour of both natural soil and soil mixture concerning maximum contaminant retention capacity.

As only one batch experiment was conducted for each soil using collected wastewater, this does not permit a more complex analysis with Langmuir isotherm (Langmuir, 1997; Appelo and Postma, 1996) that needs several batch experiments conducted with different contaminant concentrations in the inflow. The results will only be scrutinised in terms of inflow/outflow concentration comparison.

### 4.4.1. Apparatus description and methodologies

In both batch experiments the same procedure has been used. To avoid major alterations in chemical composition both natural and soil mixture were air dried. Drying in high temperatures may affect the soil organic matter composition and pH (EPA, 1992).

Concerning the soil mixture, the components described in Section 4.2.2.4 used in Column 8 and Column 9, where used in the same proportion in the batch experiment.

The adsorbent soils were mixed with SBM WWTP effluent in the proportion of 1:5 (Zakharova and Leitão, 2002) – 240 mg of soil to 1200 mg of water each. The volume of water used considered the amount of volume necessary both for pharmaceuticals (1000 mL) and other parameters (approximately 200 mL) - in the batch reactor (glass bottle).

The reactor lid was closed and the soil solution was shaken manually every hour for 12 hours during two days and after left without shaking for an additional 48 hours period. The batch reactor was kept under controlled temperature and was covered with tinfoil paper to reduce photolithotrophic microorganisms growth and photodegradation of contaminants. After settling the soil solution was filtered through 45 µm filter by vacuum pressure pumping (Figure 25). Electrical conductivity, Eh and pH effluents values have been measured and samples were sent for analysis in an external laboratory.


**Figure 25 – Batch reactor previous to water filtration**

The adsorbed amount ($Q_e$) of each heavy metal has been calculated accordingly to the following equation:

$$\boldsymbol{Q_e = \frac{(C_i - C_t) \times V}{M}}$$

where $Q_e$ represents the adsorbed amount (mg/kg), $C_i$ is the concentration before the experiment (mg/L) and $C_t$ after the experiment (mg/L), V is the volume of solution (L) and M is the mass of soil (kg).

Percent of removal (%) was calculated using the equation:

$$\% = \frac{(\boldsymbol{C_i - C_t})}{\boldsymbol{C_i}} \times \mathbf{100}$$

The parameters analysed were the same as described in Section 4.2.3. Results for natural soil and soil mixture are presented in Section 4.4.2.1.1 and 4.4.2.1.2.

### 4.4.2. Inflow/outflow results comparison

#### 4.4.2.1.1. Natural soil

Table 23 resumes the batch experiment inflow and outflow concentrations as well as the absorbed amount for each parameter analysed and the percentage of removal. For the calculations, values below LOR were considered equal to zero concentration.

**Table 23 – Natural soil batch experiment results**

| Parameter | Unit | LOR | Inflow | Outflow | Adsorbed amount (mg/kg) | Removal (%) |
|---|---|---|---|---|---|---|
| Boron | mg/L | 0.010 | 0.235 | 0.736 | **-2.505** | - |
| Copper | mg/L | 0.0020 | <0.002 | 0.0135 | **-0.0675** | - |
| Zinc | mg/L | 0.0020 | 0.0027 | 0.0054 | **-0.0135** | - |
| Ammonia | mg/L | 0.050 | 34.2 | 13.6 | 103 | 60.2 |
| Nitrates | mg/L | 2.00 | <2 | <2 | 0 | - |
| Nitrites | mg/L | 0.0050 | <0.005 | 0.175 | **-0.875** | - |
| Orthophosphate | mg/L | 0.040 | 7.68 | 1.4 | 31.4 | 81.8 |
| Sulphate | mg/L | 5.00 | 64.7 | 67 | **-11.5** | - |
| Aluminium | mg/L | 0.010 | 0.011 | <0.01 | 0.055 | 100.0 |
| Antimony | mg/L | 0.010 | <0.01 | <0.01 | 0 | - |
| Arsenic | mg/L | 0.0050 | <0.005 | <0.005 | 0 | - |
| Barium | mg/L | 0.00050 | 0.0523 | 0.474 | **-2.1085** | - |
| Beryllium | mg/L | 0.00020 | <0.0002 | <0.0002 | 0 | - |
| Cadmium | mg/L | 0.00040 | <0.0004 | <0.0004 | 0 | - |
| Calcium | mg/L | 0.0050 | 43.6 | 78.2 | **-173** | - |
| Chromium | mg/L | 0.0010 | <0.001 | 0.001 | **-0.005** | - |
| Cobalt | mg/L | 0.0020 | <0.002 | <0.002 | 0 | - |
| Iron | mg/L | 0.0020 | 0.0408 | 0.0056 | 0.176 | 86.3 |
| Lead | mg/L | 0.0050 | <0.005 | <0.005 | 0 | - |
| Lithium | mg/L | 0.0010 | 0.0012 | 0.0011 | 0.0005 | 8.3 |
| Magnesium | mg/L | 0.0030 | 29 | 37.2 | **-41** | - |
| Manganese | mg/L | 0.00050 | 0.0387 | 0.0657 | **-0.135** | - |
| Molybdenum | mg/L | 0.0020 | <0.002 | <0.002 | 0 | - |
| Nickel | mg/L | 0.0020 | 0.0021 | 0.0062 | **-0.0205** | - |
| Phosphorus | mg/L | 0.010 | 2.79 | 0.539 | 11.255 | 80.7 |
| Potassium | mg/L | 0.015 | 14.8 | 10.3 | 22.5 | 30.4 |
| Selenium | mg/L | 0.010 | <0.01 | <0.01 | 0 | - |
| Silver | mg/L | 0.0010 | <0.001 | <0.001 | 0 | - |
| Sodium | mg/L | 0.030 | 71.6 | 66 | 28 | 7.8 |
| Thallium | mg/L | 0.010 | <0.01 | <0.01 | 0 | - |
| Vanadium | mg/L | 0.0010 | <0.001 | 0.0092 | **-0.046** | - |
| Chloride | mg/L | 1.00 | 91.1 | 94 | **-14.5** | - |

Note: bold values show increase in outflow concentration

For the set of 32 parameters analysed in the inflow and outflow water, eight showed a decrease in concentration in the outflow when compared to inflow. Highest percentage of removal is observed in aluminium, followed by iron, and the lowest in sodium. Boron, copper, zinc, nitrites, sulphate, barium, calcium, chromium, magnesium, manganese, nickel, vanadium and chloride showed an increased concentration in outflow. This is the result of soil washing out and explains the increase of some elements in the outflow water, like Ba, Ni, V (Graph 9), Ca and Mg (Graph 24).

Concerning the pharmaceuticals, Table 24 resumes the inflow/outflow concentrations.

**Table 24 – Natural soil batch experiment results – pharmaceuticals**

| Parameter | Unit | LOR | Inflow | Outflow | Adsorbed amount (mg/kg) | Removal (%) |
|---|---|---|---|---|---|---|
| Atenolol | µg/L | 0.01 | 0.27 | <0.01 | 0.00135 | 100.0 |
| Betaxolol | µg/L | 0.01 | 0.01 | <0.01 | 0.00005 | 100.0 |
| Bisoprolol | µg/L | 0.01 | 0.09 | <0.01 | 0.00045 | 100.0 |
| Metoprolol | µg/L | 0.01 | 0.07 | <0.01 | 0.00035 | 100.0 |
| Pindolol | µg/L | 0.01 | <0.01 | <0.01 | 0 | - |
| Propanolol | µg/L | 0.01 | 0.05 | 0.02 | 0.00015 | 60.0 |
| Sotalol | µg/L | 0.01 | 0.08 | <0.01 | 0.0004 | 100.0 |
| Acetylsalicylic Acid | µg/L | 0.02 | <0.02 | <0.02 | 0 | - |
| Bezafibrat | µg/L | 0.02 | 0.1 | 0.07 | 0.00015 | 30.0 |
| Clofibrinsäure | µg/L | 0.02 | <0.02 | <0.02 | 0 | - |
| Diclofenac | µg/L | 0.02 | 0.48 | 0.29 | 0.00095 | 39.6 |
| Fenoprofen | µg/L | 0.02 | <0.02 | <0.02 | 0 | - |
| Gemfibrozil | µg/L | 0.02 | 0.29 | 0.24 | 0.00025 | 17.2 |
| Ibuprofen | µg/L | 0.01 | 0.06 | <0.01 | 0.0003 | 100.0 |
| Indometacin | µg/L | 0.02 | 0.03 | 0.02 | 0.00005 | 33.3 |
| Ketoprofen | µg/L | 0.01 | <0.01 | <0.01 | 0 | - |
| Naproxen | µg/L | 0.01 | 0.56 | 0.54 | 0.0001 | 3.6 |
| Carbamazepin | µg/L | 0.01 | 0.48 | 0.3 | 0.0009 | 37.5 |
| Diazepam | µg/L | 0.01 | <0.01 | <0.01 | 0 | - |
| Etofibrat | µg/L | 0.02 | <0.02 | <0.02 | 0 | - |
| Fenofibrat | µg/L | 0.04 | <0.04 | <0.04 | 0 | - |
| Pentoxifyllin | µg/L | 0.01 | 0.24 | <0.01 | 0.0012 | 100.0 |
| Phenacetin | µg/L | 0.01 | <0.01 | <0.01 | 0 | - |
| Phenazon | µg/L | 0.01 | <0.01 | <0.01 | 0 | - |

While in inflow water 14 of 24 pharmaceuticals had values above LOR, only seven of those were persistent and were detected in the outflow (propanolol, bezafibrate, diclofenac, gemfibrozil, naproxen, indometacin and carbamazepine). For the persistent compounds, lowest removal rate was detected for naproxen. Seven of the 24 pharmaceuticals showed 100% removal (atenolol, betaxolol, bisoprolol, metoprolol, sotalol e pentoxifillin).

#### 4.4.2.1.2. Soil mixture

Concerning soil mixture batch experiment results, Table 25 resumes the inflow/outflow concentrations as well as removal rates.

**Table 25 - Soil mixture batch experiment results**

| Parameter | Unit | LOR | Inflow | Ouflow | Adsorbed amount (mg/kg) | Removal (%) |
|---|---|---|---|---|---|---|
| Boron | mg/L | 0.010 | 0.723 | 0.111 | 3.06 | 84.6 |
| Copper | mg/L | 0.0020 | 0.0033 | 0.0038 | **-0.0025** | - |
| Zinc | mg/L | 0.0020 | 0.0049 | 0.0062 | **-0.0065** | - |
| Ammonia | mg/L | 0.050 | 48.9 | 26 | 114.5 | 64.0 |
| Nitrates | mg/L | 2.00 | <2 | <2 | 0 | - |
| Nitrites | mg/L | 0.0050 | <0.0104 | 0.248 | **-1.188** | - |
| Orthophosphate | mg/L | 0.040 | 15.2 | 9.96 | 26.2 | 43.7 |
| Sulphate | mg/L | 5.00 | 70.9 | 68 | 14.5 | 4.1 |
| Aluminium | mg/L | 0.010 | 0.057 | <0.01 | 0.285 | 100.0 |
| Antimony | mg/L | 0.010 | 0.083 | <0.01 | 0.415 | 100.0 |
| Arsenic | mg/L | 0.0050 | <0.005 | 0.005 | **-0.025** | - |
| Barium | mg/L | 0.00050 | 0.18 | 0.162 | 0.09 | 10.0 |
| Beryllium | mg/L | 0.00020 | <0.0002 | <0.0002 | 0 | - |
| Cadmium | mg/L | 0.00040 | <0.0004 | <0.0004 | 0 | - |
| Calcium | mg/L | 0.0050 | 37.8 | 71.4 | **-168** | - |
| Chromium | mg/L | 0.0010 | 0.0022 | 0.0016 | 0.003 | 27.3 |
| Cobalt | mg/L | 0.0020 | <0.002 | <0.002 | 0 | - |
| Iron | mg/L | 0.0020 | 0.0634 | 0.0111 | 0.2615 | 82.5 |
| Lead | mg/L | 0.0050 | <0.005 | <0.005 | 0 | - |
| Lithium | mg/L | 0.0010 | 0.0167 | 0.0164 | 0.0015 | 2.0 |
| Magnesium | mg/L | 0.0030 | 28.4 | 28.7 | **-1.5** | - |
| Manganese | mg/L | 0.00050 | 0.0572 | 0.203 | **-0.729** | - |
| Molybdenum | mg/L | 0.0020 | 0.0024 | <0.002 | 0.012 | 100.0 |
| Nickel | mg/L | 0.0020 | 0.0069 | 0.0025 | 0.022 | 63.8 |
| Phosphorus | mg/L | 0.010 | 5.52 | 3.25 | 11.35 | 52.4 |
| Potassium | mg/L | 0.015 | 23.6 | 31.8 | **-41** | - |
| Selenium | mg/L | 0.010 | 0.027 | <0.01 | 0.135 | 100.0 |
| Silver | mg/L | 0.0010 | 0.0013 | <0.001 | 0.0065 | 100.0 |
| Sodium | mg/L | 0.030 | 92.5 | 82.9 | 48 | 12.2 |
| Thallium | mg/L | 0.010 | 0.074 | <0.01 | 0.37 | 100.0 |
| Vanadium | mg/L | 0.0010 | 0.0055 | <0.001 | 0.0275 | 100.0 |
| Chloride | mg/L | 1.00 | 118 | 121 | **-15** | - |

Note: bold values show increase in outflow concentration

From the 32 parameters considered, 25 were detected in inflow water while only 20 were detected in the outflow water. Ammonia presented the highest adsorbed amount and copper, zinc, nitrites, calcium, magnesium, manganese, potassium and chloride showed an increase of concentration in outflow. For this set of parameters percentage of removal was higher in antimony, aluminium, molybdenum, selenium, silver, thallium and vanadium, and lowest in lithium. Again this increase in the outflow water is a result from the interaction between soil and water and explains the increase observed in Graph 47 until S11 (since the increase in concentration after that period have different reasons). The capacity to retain Ba is also clearly seen for this soil mixture when compared to the natural soil.

Concerning pharmaceuticals results are presented in Table 26.

**Table 26 – Soil mixture batch experiment results – pharmaceuticals (values in red are below LOR)**

| Parameter | Unit | LOR | Inflow | Ouflow | Adsorbed amount (mg/kg) | Removal (%) |
|---|---|---|---|---|---|---|
| Atenolol | µg/L | 0.01 | 0.06 | <0.01 | 0.0003 | 100.0 |
| Betaxolol | µg/L | 0.01 | 0.01 | <0.01 | 0.00005 | 100.0 |
| Bisoprolol | µg/L | 0.01 | 0.03 | <0.01 | 0.00015 | 100.0 |
| Metoprolol | µg/L | 0.01 | 0.04 | <0.01 | 0.0002 | 100.0 |
| Pindolol | µg/L | 0.01 | <0.01 | <0.01 | 0 | - |
| Propanolol | µg/L | 0.01 | 0.02 | <0.01 | 0.0001 | 100.0 |
| Sotalol | µg/L | 0.01 | 0.05 | <0.01 | 0.00025 | 100.0 |
| Acetylsalicylic Acid | µg/L | 0.02 | <0.02 | <0.02 | 0 | - |
| Bezafibrat | µg/L | 0.02 | 0.01 | <0.01 | 0.00005 | 100.0 |
| Clofibrinsäure | µg/L | 0.02 | <0.02 | <0.02 | 0 | - |
| Diclofenac | µg/L | 0.02 | 0.15 | <0.01 | 0.00075 | 100.0 |
| Fenoprofen | µg/L | 0.02 | <0.02 | <0.02 | 0 | - |
| Gemfibrozil | µg/L | 0.02 | 0.4 | <0.02 | 0.002 | 100.0 |
| Ibuprofen | µg/L | 0.01 | 0.01 | <0.01 | 0.00005 | 100.0 |
| Indometacin | µg/L | 0.02 | 0.02 | <0.02 | 0.0001 | 100.0 |
| Ketoprofen | µg/L | 0.01 | <0.01 | <0.01 | 0 | - |
| Naproxen | µg/L | 0.01 | 0.17 | <0.01 | 0.00085 | 100.0 |
| Carbamazepin | µg/L | 0.01 | 0.73 | 0.1 | 0.00315 | 86.3 |
| Diazepam | µg/L | 0.01 | <0.01 | <0.01 | 0 | - |
| Etofibrat | µg/L | 0.02 | <0.02 | <0.02 | 0 | - |
| Fenofibrat | µg/L | 0.04 | <0.04 | <0.04 | 0 | - |
| Pentoxifyllin | µg/L | 0.01 | 0.01 | <0.01 | 0.00005 | 100.0 |
| Phenacetin | µg/L | 0.01 | <0.01 | <0.01 | 0 | - |
| Phenazon | µg/L | 0.01 | <0.01 | <0.01 | 0 | - |

For the selected 24 pharmaceuticals analysed, 14 were above LOR in inflow water and only 1 in the outflow water. 100% removal rate was observed in atenolol, betaxolol, bisoprolol, metoprolol, propranolol, sotalol, bezafibrate, diclofenac, gemfibrozil, ibuprofen, indomethacin, naproxen and pentoxifyllin. Carbamazepine showed recalcitrant behaviour, but a relatively high removal rate (86.3%).

# 5. Numerical modelling of column experiments

Numerical modelling exercises were conducted using data collected in the soil-column experiments. These exercises can be a helpful tool to describe contaminants behaviour as well as some removal mechanisms and the conditions in which they occur. Solute transport and geochemical modelling were considered for the column behaviour understanding.

For the solute transport modelling Hydrus-1D (Jacques and Šimůnek, 2005) was used. This software is widely used to simulate flow and solute transport in variably saturated soils and groundwater in both steady and transient state. One dimensional flow can be modelled at different scales from laboratory soil-columns to larger experiments. Hydrus-1D can also considerer inverse problems when some parameters need to be calibrated or estimated from observed data.

For geochemical modelling PHREEQC 3.1 (Parkhurst and Appelo, 2013) was used. PHREEQC is a speciation program to calculate the saturation index for numerous minerals and solid phases, the distribution of aqueous species in equilibrium, as well as the density and specific conductance of a specified solution composition. Also adsorption and desorption can be modelled as surface complexation reactions or as ion exchange reactions as well as ion exchange.

HP1 (Hydrus-1D coupled with PHREEQC) package was not used, as it was not fundamental for the modelling process. Compared to HP1, PHREEQC 3.1 interactive menus and capabilities allow for easier and faster inclusion of large amounts of data, while the first software requires the user to have deeper knowledge of input language and data insertion, which is not as intuitive. Also, PHREEQC 3.1 allows for easier output data selection and integration with other software like Excel.

In these modelling exercises pharmaceuticals where not considered due to the complexity of the modelling processes and the large number of influencing factors. Few studies have attempted to model this type of compound breakthroughs curves to differentiate between sorption and biodegradation, as modelling does not take into account the main removal mechanisms and considers the results as a whole trying to relate some changes with some initial varying conditions (DEMEAU, 2015).

## 5.1. Nitrogen cycle / transport modelling

### 5.1.1. Input data

Given that nitrogen cycle is highly dependent on redox conditions, modelling the nitrification process can be useful to understand the conditions inside the column.

For this modelling process, continuous saturated conditions were considered – all time length of Column 3 experiment (continuous flow) and the first saturation cycle of Column 4. Column 5 was not modelled due to the small number of outflow samples. Column 8 was also not considered taking into account that no data was available granulometric percentages for the soil mixture, which is necessary input data for Hydrus-1D.

Simulations were run in transient state for solute transport, where the inflow and outflow concentrations were considered as solute top and bottom boundary conditions respectively. Both models were divided into five time intervals.

Input parameters for both soil-column experiments are presented in Table 27. Some of the input parameters were obtained by bibliographic research while others were inverse modelled (Ilie, 2015).

**Table 27 – Input data for Hydrus-1D C3 and C4 models.**

| Parameter | | Column 3 | Column 4 | Ref. | Observations |
|---|---|---|---|---|---|
| Depth of the soil profile (cm) | | 20 | 30 | - | - |
| Total time (min) | | 6131 | 3084 | - | - |
| Time-variable boundary conditions | | 12 | 8 | - | - |
| Soil parameters | Bulk density ($g/cm^3$) | 1.44 | 1.52 | Ilie (2015) | Determined by Rosetta Lite v1.1 from soil granulometry without considering > 2 mm fraction (clay = 78.51%; silt = 18.96%; sand = 2.53%) |
| | Qr | 0.0368 | 0.0364 | | |
| | Qs | 0.3907 | 0.3704 | | |
| | Alpha (1/cm) | 0.0446 | 0.0457 | | |
| | n | 1.7305 | 1.7596 | | |
| | Ks (cm/min) | 0.1011 | 0.0798 | | |
| Boundary condition | Upper | Constant pressure head (20 cm) | Constant pressure head (30 cm) | - | - |
| | Lower | Free drainage | | - | - |
| Solute parameters | Long. Dispersivity | 2 | 2 | Simuneck *et al.* (2013) | - |
| | Diffus. Water. | 0.000833 | 0.000833 | Ramos and Carbonell (1991) | - |
| | Reaction parameters | Inverse solution modelling | | Ilie (2015) | - |
| Solute transport boundary cond. | Upper | Concentration flux BC | | - | - |
| | Lower | Zero concentration gradient | | - | - |

### 5.1.2. Results

Simulations were successful and the model converged to a solution. Model results of both columns for the solutes are presented in Figure 26.

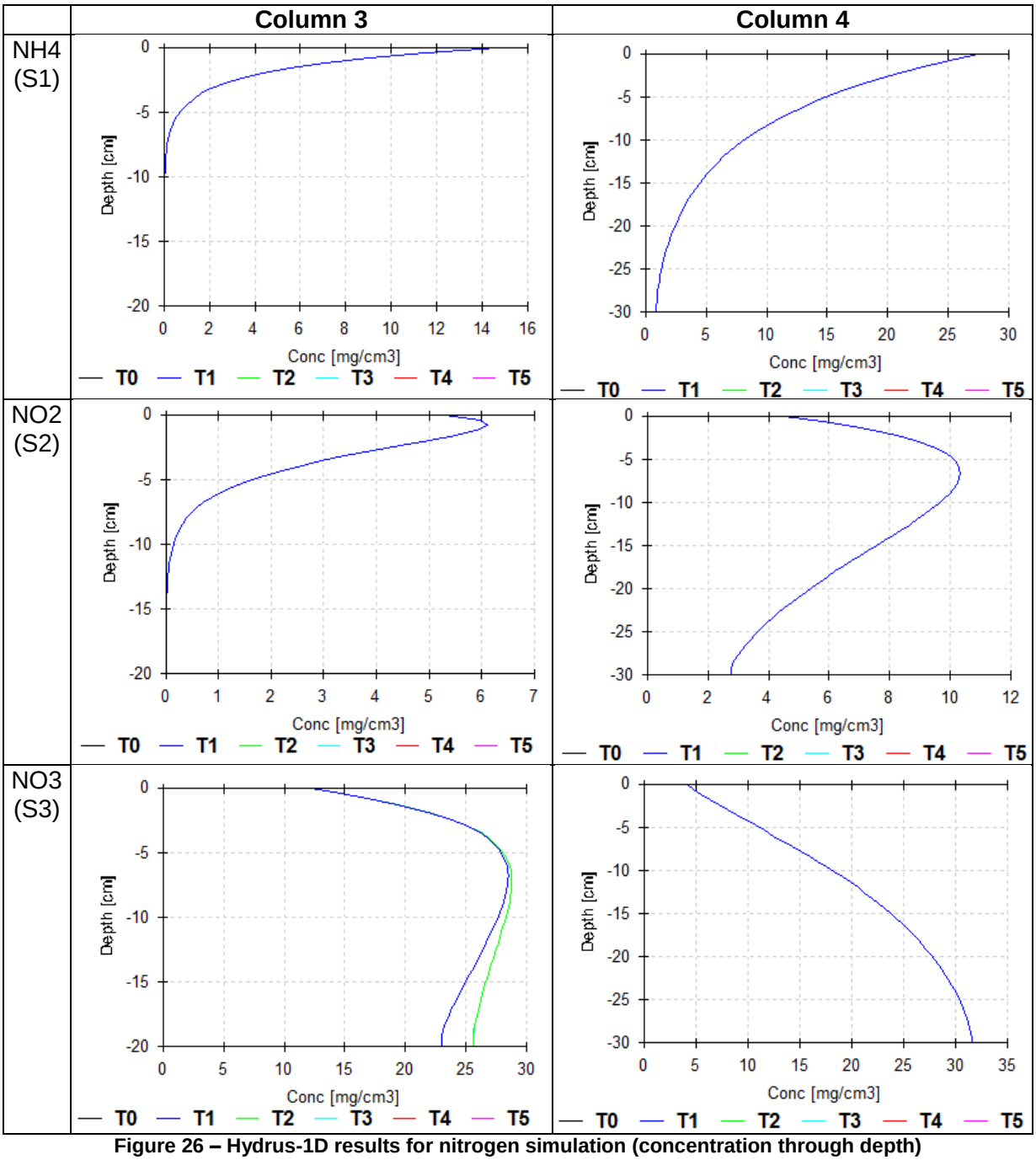



**Figure 26 – Hydrus-1D results for nitrogen simulation (concentration through depth)**

Both simulations show similar behaviour along the columns, with ammonia being mostly existing (and retained) on the top of the column whereas nitrites show a small increase in concentration as ammonia is oxidized to nitrite, and then nitrites decrease at the column bottom as they are transformed into nitrates. In Column 3 simulation, ammonia concentration rapidly decreases to zero at the first half of the column while in Column 4 some ammonia can be observed at the bottom section but in much lower concentration than that observed on the top. Nitrites concentrations show a small increase in the first centimetres of the column top and decreases again. In Column 4 bottom nitrites are observed at the outflow. Nitrates continuously increase in Column 4 while in Column 3

this compound increases at the first ¼ of the column thickness and slowly decreases after that.

For the considered parameters for the three solutes, solute retention and possibly transformation can be observed, which can suggest that good conditions occur at the columns for nitrification, with lower oxygen content on the column top and slight oxygenation on the bottom (where higher concentration of nitrates is observed).

Although ammonia retention on the column is confirmed by inflow and outflow comparison, particularly in natural soil experiments (C3 to C5), the observed behaviour calculated in simulations is not what is observed in the soil-column experiments results, mainly for nitrates concentrations. In soil-columns, nitrates show low concentration at outflow, instead of high concentrations calculated in the model. This may result from the time of simulation considered, but also, in the soil columns, to a process of retention of nitrates, observed in the models, where nitrates have high concentrations at the bottom section of the column and possibly are not mobilized to the water.

Five nodes were represented along both columns, equally distributed between them. Results for variation of concentration through time taken from these nodes (from top to bottom) are presented in Figure 27 and Figure 28.

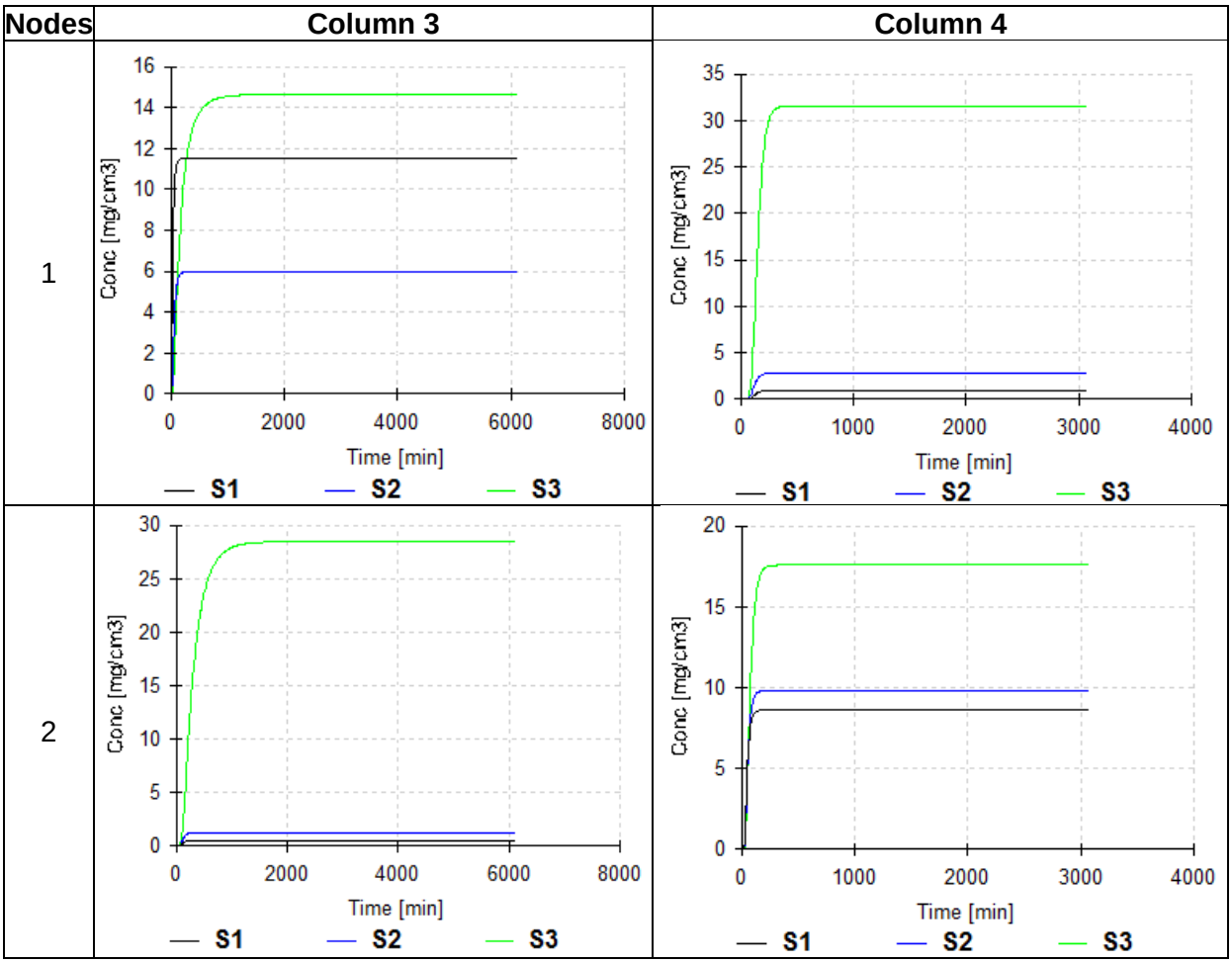



**Figure 27– Hydrus-1D results for nitrogen simulation for node 1and 2 (S1 – ammonia, S2 – nitrites, S3 – nitrates)**

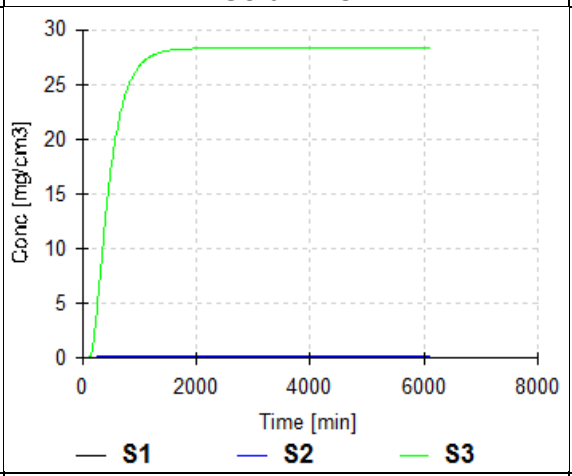
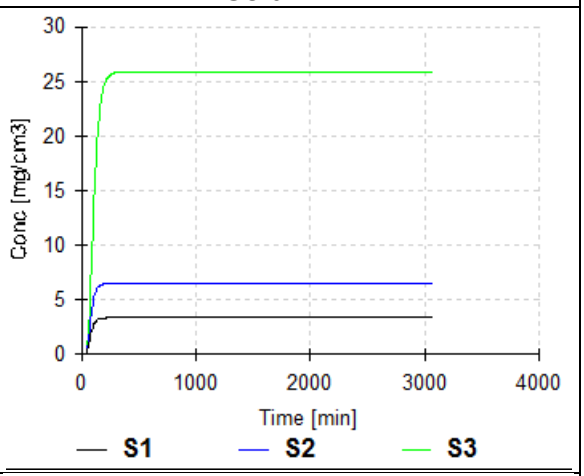
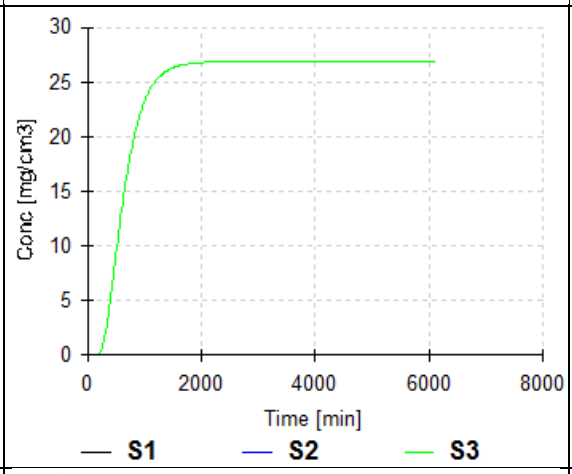
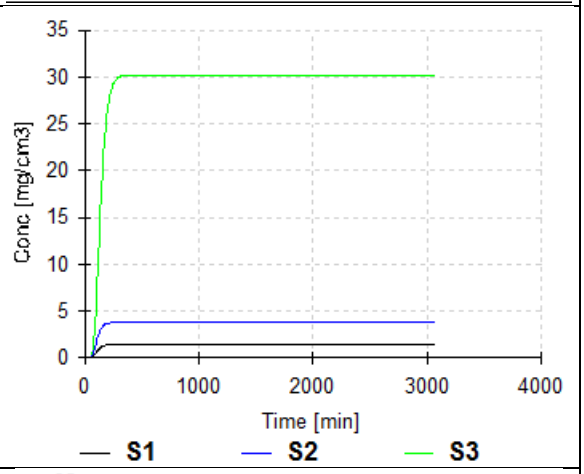
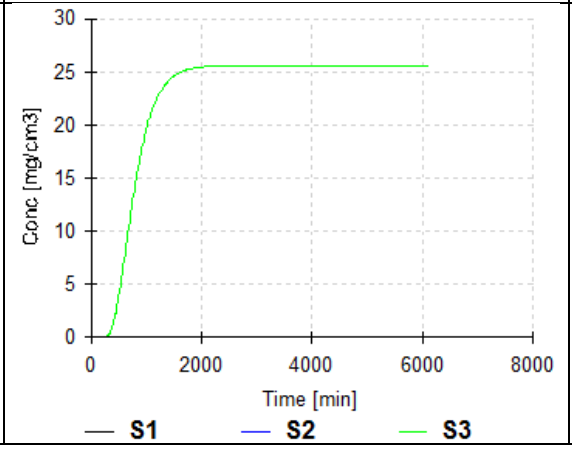
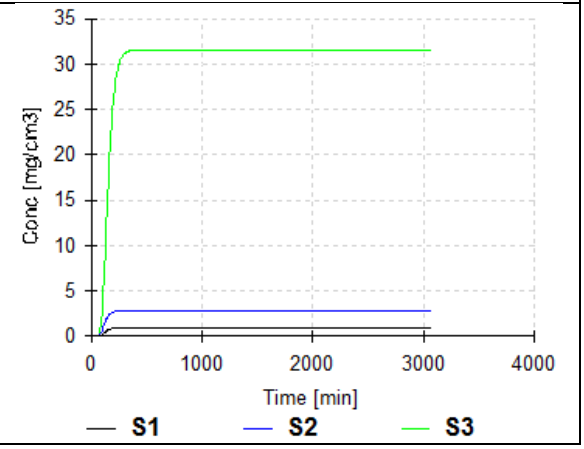
| Nodes | Column 3 | Column 4 |
|---|---|---|
| 3 |  |  |
| 4 |  |  |
| 5 |  |  |

**Figure 28– Hydrus-1D results for nitrogen simulation for nodes 3, 4 and 5 (S1 – ammonia, S2 – nitrites, S3 – nitrates)**

Solute behaviour is observed in different depths along the columns, through time (from point 1 to 5). Again ammonia (S1) concentrations are very low (or null) at the bottom in both columns.

In an overview of the model results, Column 3 achieves stabilization in these compounds concentration in the first 1000 minutes and in Column 4 at approximately 200 minutes. If

pore-volumes determined in soil-column experiments are considered and that 1L of water is injected in both columns (steady state flow), these periods correspond to 5.7PV for C3 and 3.8PV for C4.

## 5.2. Saturation index / Hydrogeochemical modelling

### 5.2.1. Input data

Taking into account the relatively high outflow concentrations of calcium and magnesium, the Saturation Index (Log SI) was calculated for calcite and dolomite. Considering that hematite is one of the natural soil constituents (as presented in Section 4.3.1.1) its Log SI was also determined. Given that there are no determination of silica, both at outflow and inflow for all columns, the calculation of Log SI for the other major mineral constituents of the natural soil was not possible (quartz, anorthite, montmorillonite, kaolinite, etc.).

Column 3, Column 4 and Column 8 inflow and outflow solutions were inserted into PHREEQC. Column 5 was not considered due to the small number of outflow samples.

As $HCO_3^-$ concentration was only measured for Column 8 inflow and outflow, average concentration detected at C8 outflow was used as input for Column 3 and Column 4. Inflow concentration of this parameter was also used as input for inflow solution for C3 and C4

PHREEQC input data is presented in Appendix 5.

### 5.2.2. Results

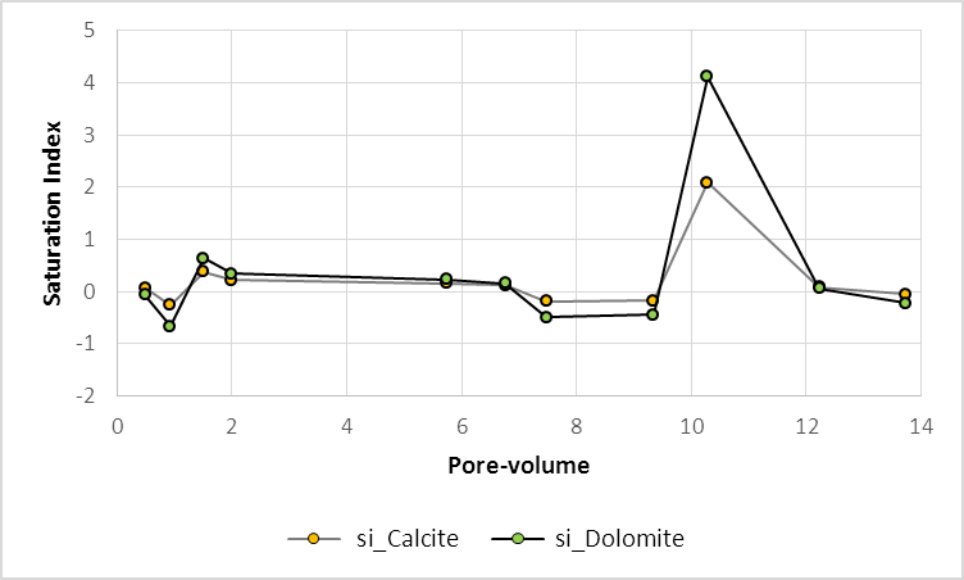
Saturation indexes determined for dolomite, calcite and hematite for Column 3 inflow solution are presented in Table 28.

**Table 28 – Column 3 inflow Log SI for dolomite, calcite and hematite**

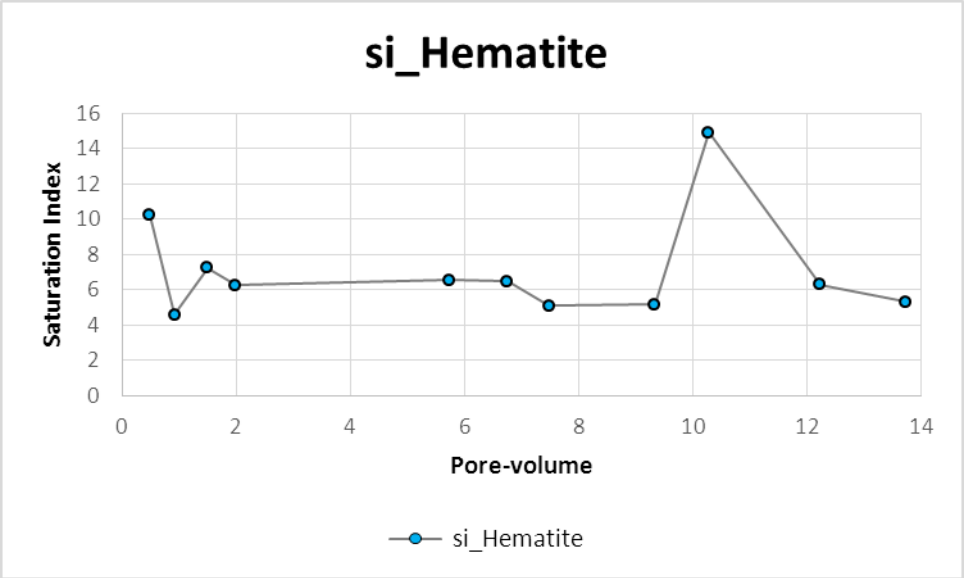
| | Dolomite | Calcite | Hematite |
|---|---|---|---|
| Saturation Index (Log) | -3.8967 | -1.9426 | 0.2011 |

The Log SI calculated shows that Column 3 inflow water is unsaturated in calcite and dolomite. Very low value (Log SI ≈ 0) for hematite show that the solution is in equilibrium with this mineral.

Saturation index for calcite and dolomite of Column 3 outflow is presented in Graph 55. Hematite saturation index is presented in Graph 56.




**Graph 55 – Column 3 outflow Log SI for calcite and dolomite**




**Graph 56 – Column 3 outflow Log SI for hematite**

Both calcite, dolomite and hematite present similar behaviour although Log SI for hematite is slightly higher. Outflow Log SI shows that solution is saturated in these minerals until PV7, where unsaturated suggests that conditions inside the column changed. At approximately PV10 Log SI for the set of minerals is positive, decreases to equilibrium state and unsaturated again.

Unsaturation at inflow and saturation at outflow suggests that calcite and dolomite dissolution is occurring inside the column. Therefore, these results can explain the large concentrations of Ca and Mg at the outflow.

High pH measured in solution 11 (near PV10) may have resulted in relatively high Log SI for hematite, calcite and dolomite.

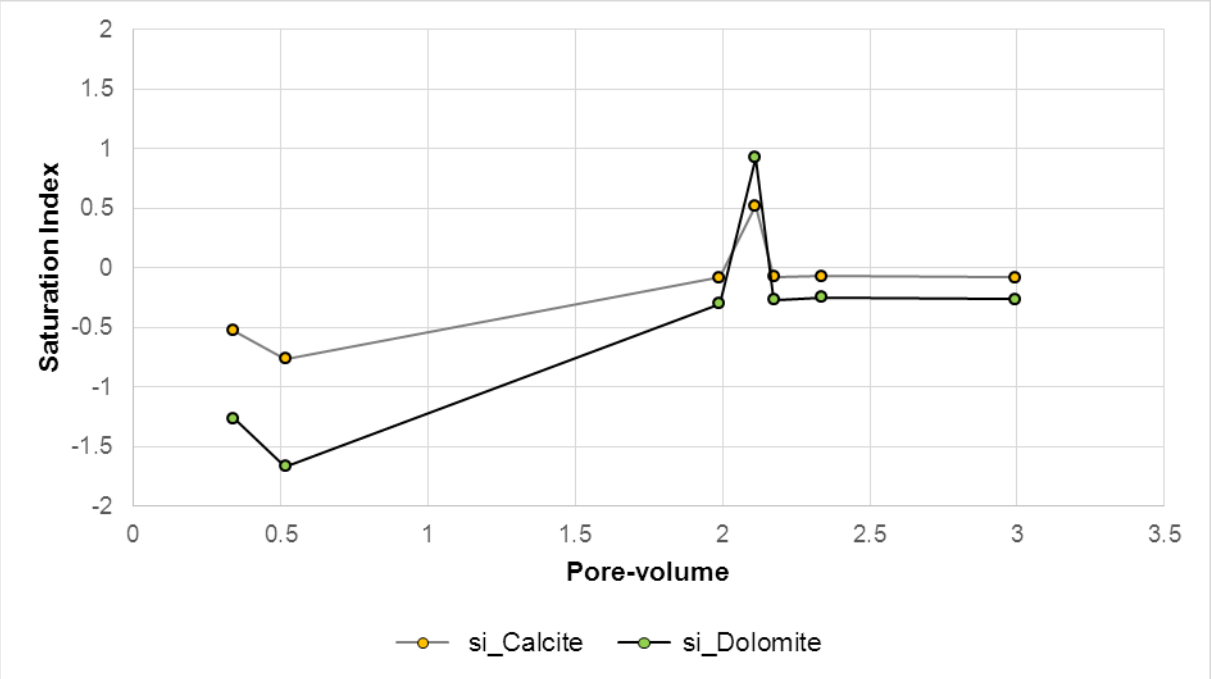
Saturation indexes determined for dolomite, calcite and hematite for Column 4 inflow solution are presented in Table 29.

**Table 29 – Column 4 inflow Log SI for dolomite, calcite and hematite**

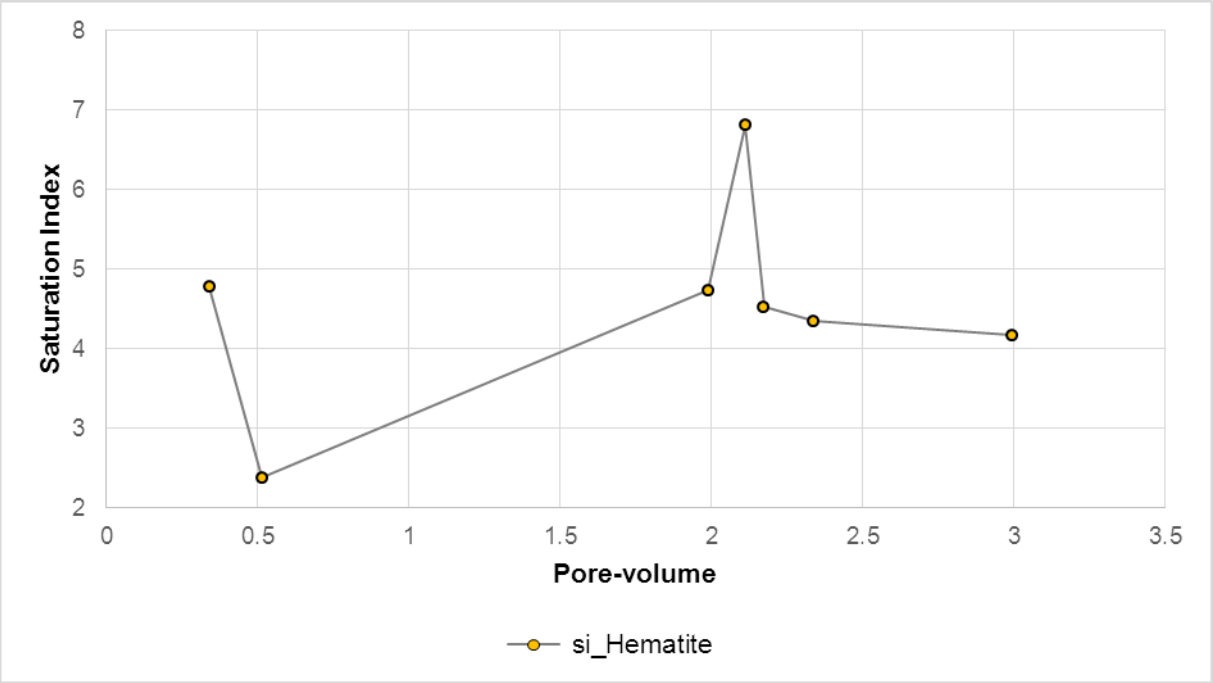
| | Dolomite | Calcite | Hematite |
|---|---|---|---|
| Saturation Index (Log) | 0.0298 | 0.0281 | 14.6752 |

In this soil-column experiment, inflow solution is close to stability concerning dolomite and calcite while high Log SI for hematite was determined, showing saturation in this iron oxide.

Saturation index for calcite and dolomite in Column 4 outflow is presented in Graph 57. Hematite saturation index is presented in Graph 58.




**Graph 57 – Column 4 outflow Log SI for calcite and dolomite**




**Graph 58 – Column 4 outflow Log SI for hematite**

Again, Column 4 Log SI for calcite, dolomite and hematite seem to follow the same behaviour. Outflow Log SI for calcite and dolomite is constantly below 0, showing that the solution collected at column outlet is unsaturated in these minerals (except of PV2 where Log SI ≈ 1). On the other hand, hematite Log SI is constantly over 0, showing saturation, although Log SI is much lower than Log SI calculated for inflow. This can suggest that Column 4 conditions allowed for some precipitation of these minerals, instead of dissolution. It's also important to note that this data is referring to only 3 pore-volumes of the experiment.

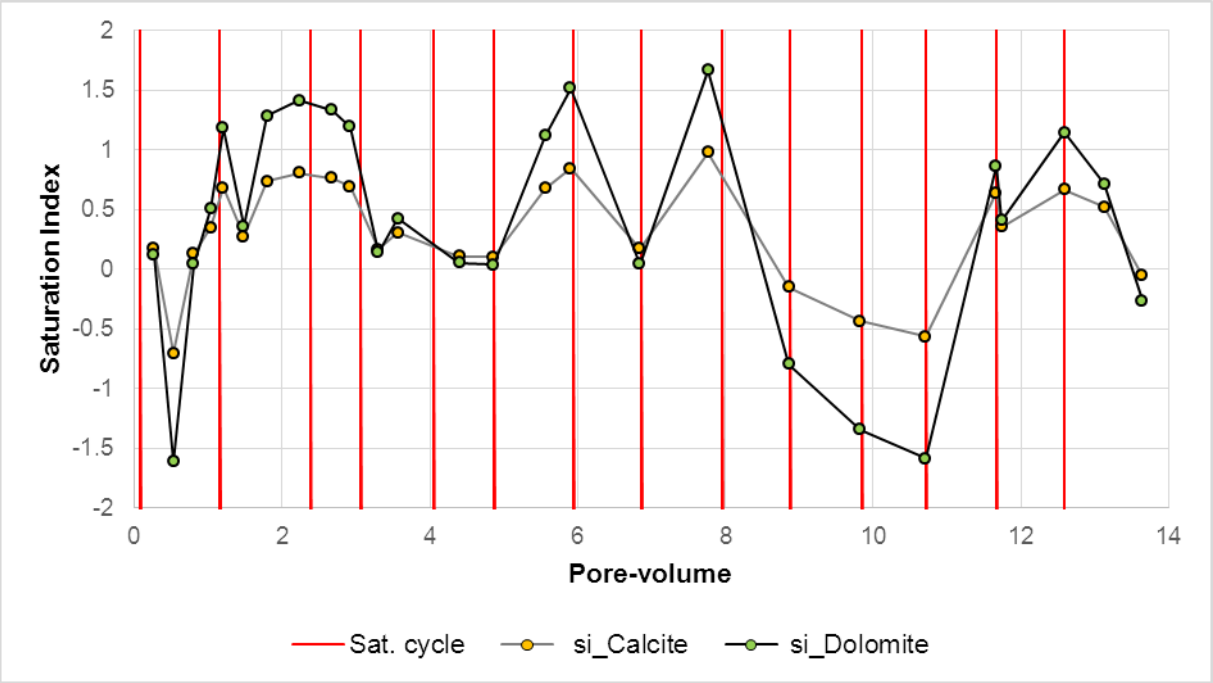
Saturation indexes determined for dolomite, calcite and hematite for Column 8 soil mixture inflow solution are presented in Table 30.

**Table 30 – Column 8 inflow Log SI for dolomite, calcite and hematite**

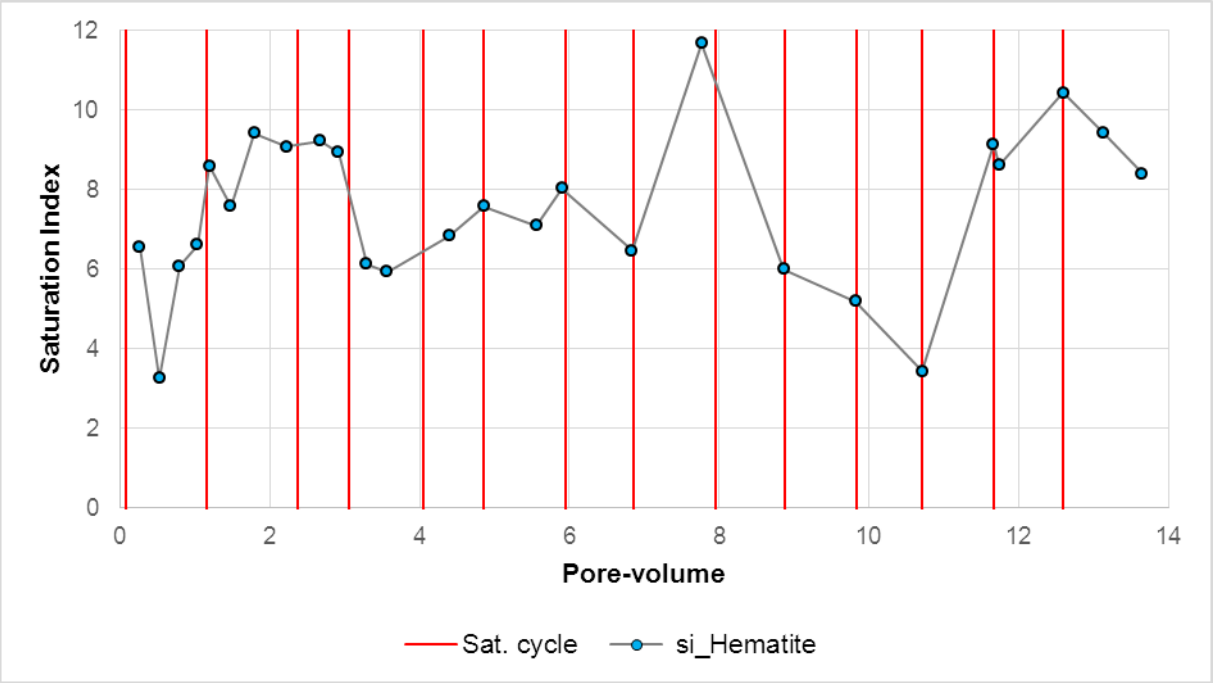
| | **Dolomite** | **Calcite** | **Hematite** |
|---|---|---|---|
| Saturation Index (Log) | -0.4131 | -0.2777 | 11.2803 |

For this soil-column experiment, inflow solution is slightly unsaturated in calcite and dolomite. Again hematite Log SI is showing oversaturation at inflow.

Saturation index for calcite and dolomite of Column 8 outflow is presented in Graph 59. Hematite saturation index is presented in Graph 60.




**Graph 59 – Column 8 outflow Log SI for calcite and dolomite**




**Graph 60 – Column 8 outflow Log SI for hematite**

Column 8 outflow Log SI general behaviour shows that, except for a small period after experiment start and PV9-11, Log SI for calcite and dolomite is >0. Taking in account that inflow was unsaturated in these minerals, dissolution occurred inside the column. Again this can explain the high concentrations of Ca and Mg at outflow. Saturation cycles seem to result in an increase of SI, suggesting that mineral dissolution inside the column

starts as soon as spreading starts. Interval between PV9 and PV11 suggest that conditions inside the column changed as calcite and dolomite are unsaturated. Temperature values measured for the samples collected between this interval were relatively low (<10ºC) which could have resulted in low Log SI in speciation modelling.

Concerning hematite, Log SI values calculated for C8 outflow solutions, which are very similar to inflow SI, show once again saturation. It is possible that hematite in the soil constitution remains unchanged, and no reactions occur between the soil media and solution concerning this mineral. Besides this, there is a difference between inflow and outflow concentration of iron for the soil mixture experiment (Section 4.3.2.3.1).

## 5.3. Inverse modelling

### 5.3.1. Input data

Inverse modelling was used as a way to understand phase transfers that occur between inflow solution and the soil media. The methodology adopted consisted in inverse modelling solution A to solution B, C, D, etc., having as solution A the initial solution – the inflow water – and the final solutions as the outflow solutions collected from the column.

For this exercise, Column 3 results were used, considering that the experiment was conducted in continuous flow/saturation cycle (meaning that no changes in terms of conditions were induced directly in the column) and also the substantial number of samples collected at outflow.

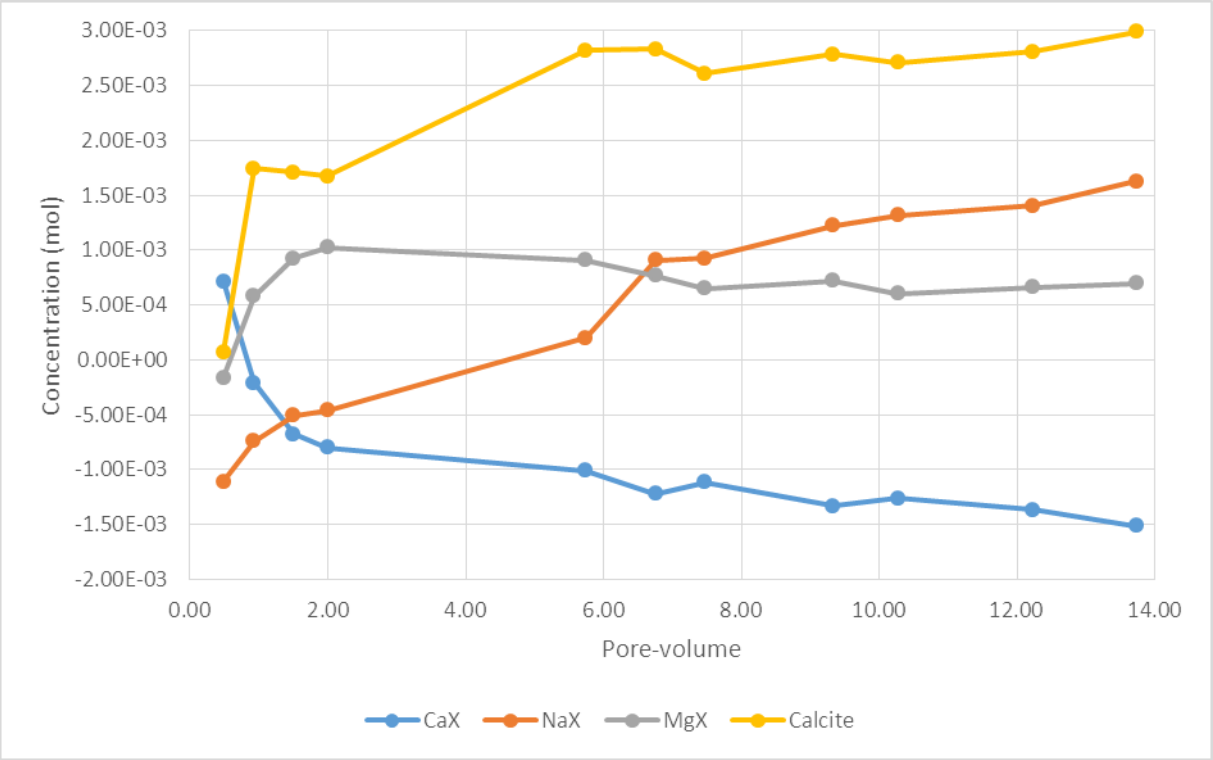
Three of the major ions that show significant concentrations at outflow and are major constituents of the minerals in the natural soil – calcium, magnesium and sodium. As input, two mineral phases – calcite and dolomite – and three exchangers – CaX2, MgX2 and NaX – were considered. Mineral phases mass transfers between initial to final solutions allow to understand if dissolution or precipitation processes occur. Exchangers present cation exchange processes.

This inverse modelling approach can represent a simple way to understand the behaviour of soil concerning retention of certain ions giving column outflow concentrations.

### 5.3.2. Results

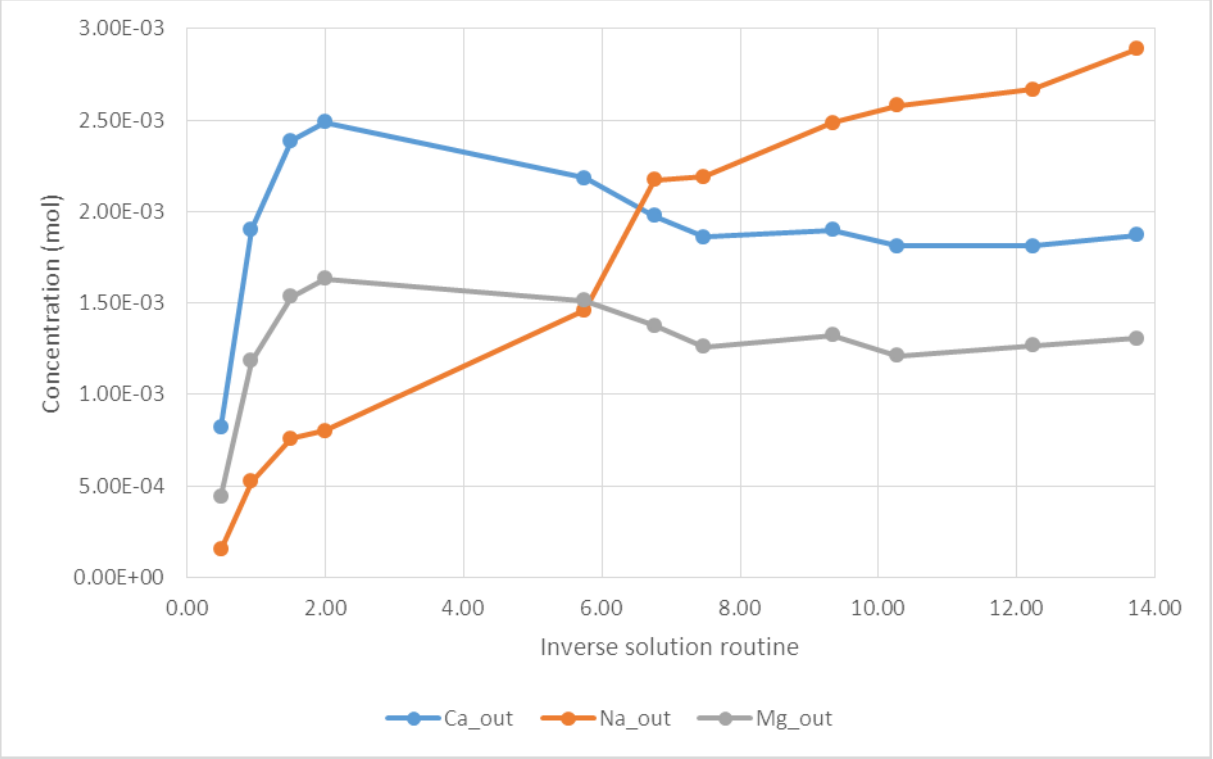
Results for Inverse Modelling process ran through PHREEQC are presented in Graph 61.

It’s important to refer that for mineral phases, positive values of concentration means dissolution in the second solution (outflow), as this is enriched in that element when compared to the first solution (inflow). For the exchangers (CaX2, NaX and MgX2), negative values in concentration means that it gave ions to the solution, enriching the solution in the element of the exchanger.




**Graph 61 – Column 3 results for inverse modelling phases**

For comparison purposes, concentrations at outflow (in mols) for the selected set of ions are presented in Graph 62.




**Graph 62 – Column 3 outflow concentrations of ions considered in inverse modelling process**

Concerning the mineral phases analysed, inverse models where dolomite dissolution/precipitation occurs weren't considered, being given special attention to models that considered calcite and exchangers. This decision results from the fact that it is very unlike to occur dolomite precipitation or dissolution in such a small column.

In terms of processes that occur in the column for inflow solution to become outflow solutions, it's possible to observe a positive phase transfer of calcite from the initial solution to final solutions. It can be assumed that continuous dissolution of this mineral is occurring, and it's especially important in the first pore-volume. On the other hand an inverse behaviour is calculated for calcium exchanger, resulting negative phase transfers to it and therefore an enrichment of the solution concentrations at outflow. Considering that inflow water composition does not vary throughout the experiment, it can be assumed that calcite dissolution and calcium washout occur, therefore large concentrations are encountered in outflow solutions. This continuous dissolution can be a positive factor in the retention of contaminants, such as metals.

Calcium concentrations at outflow increase rapidly in the first two PV, and after that slowly decreases and seams to stabilize. Mineral phase (calcite) and calcium exchanger also follow similar behaviour.

Magnesium and sodium exchangers seam to follow the exact pattern as outflow concentrations, but while magnesium exchanger tends to stabilize in positive phase transfers, slowly retaining this element, sodium exchanger shows an increasing trend (positive phase transfers) for retention. This is somewhat contrary to what was expected.

Continuously high outflow concentrations of Mg and Na when compared to inflow can be explained by dissolution of other phases that were not considered in this analysis. If silica concentration at both inflow and outflows was measured clay minerals interaction with inflow solution could be modelled (when considering additional mineral phases such as montmorillonite or illite).

# 6. Results discussion

Considering the soil characteristics, and comparing both natural and soil mixtures it's expected, due to the components used, that the later presents increased composition in carbonates and organic matter. Both are expected to have significant effects in terms of contaminant degradation and retention. Also, the increase in granulometry, by addition of artificial sand component (with granulomectric composition of approximately 98% above 0.063 mm) resulted in an increase of flow rates at outflow, and therefore an increase in permeability. This may also help in facing the possible long term effects of soil washout processes resulting from the addition of organic soil. Column 6 (40% of organic soil) and Column 7 (30% of organic soil) showed a significant decrease in thickness resulting from particle washout processes (up to 3 cm in approximately 4 days of functioning). This was actually observed in the outflow water colour (slightly yellow). This was not relevant in Column 8 and Column 9 where the decrease of organic soil percentage and increase of artificial sand component gave structure to the soil mixture, lessening the washout process.

In terms of soil behaviour, the soil mixture presents similar behaviour to natural soil concerning the response to saturation cycles, with a rapid increase of flow rate and decreasing as water above soil top is depleted. Besides that, soil mixture generally showed higher results concerning permeability, both in short term (1 day) and long term periods – Table 31.

**Table 31 – General summary of soil behaviour results**

| | | C1 | C2 | C3 | C4 | C5 | C6 | C7 | C8 | C9 |
|---|---|---|---|---|---|---|---|---|---|---|
| **Experiment time length (days)** | | 1 | 0.11 | 4.26 | 32.99 | 15.92 | 4 | 4 | 46 | 46 |
| **Flow rate ($cm^3/min$)** | **Day 1** | 0.846 | - | 0.869 | 0.363 | 1.504 | 7.722 | 2.572 | 3.340 | 4.341 |
| | **Experiment time** | 0.846 | 1.457 | 0.789 | 0.174 | 0.543 | 4.931 | 1.789 | 0.792 | 1.272 |
| **Permeability (m/d)** | **Day 1** | 1.353 | - | 1.445 | 0.589 | 2.536 | 12.579 | 3.557 | 3.278 | 4.562 |
| | **Experiment time** | 1.353 | 2.480 | 1.312 | 0.282 | 0.915 | 8.032 | 2.474 | 0.777 | 1.337 |

Considering the columns where quality component was analysed, C8 and C9 showed good results in long term behaviour as both experiments were conducted for 46 days. C4 showed the worst results in both short and long time behaviour. Although several processes could have led to these results in this soil-column experiment, packing process of natural soil and immediate injection of wastewater are the apparent causes if compared with Column 5 results (only two packing strikes instead of three and first cycle was conducted with deionized water). This behaviour is consistent to Pavelic *et al.* (2011) that observed high dependence of hydraulic loading rates on the level of treatment given to the source water (in particular, to the level of particles present in the source water) and subsequent clogging effects.

In general terms, the permeability decrease is faster in the natural soil and total clogging was even observed in C4. C8 and C9 were still functioning after more than 1 month, although with smaller outflow, which shows a good behaviour for an infiltration basin.

Metal concentration results comparison between natural soil (C3, C4 and C5) and soil mixture (C8 and C9) are presented in Table 32. Outflow values (OUT) represent the average concentration measured in each outflow sample.

**Table 32 – Metals and metalloids results comparison (mg/L)**

| | Parameter | Column 3 | | Column 4 | | Column 5 | | Column 8 | |
|---|---|---|---|---|---|---|---|---|---|
| | | IN | OUT | IN | OUT | IN | OUT | IN | OUT |
| Metals | Aluminium | 0.0140 | 0.0287 | 0.0110 | 0.0110 | 0.0110 | 0.0149 | 0.0570 | 0.0179 |
| | Antimony | - | - | - | - | - | - | 0.0830 | 0.0194 |
| | Barium | 0.0673 | 0.2431 | 0.0523 | 0.4855 | 0.0523 | 0.4420 | 0.1800 | 0.3753 |
| | Boron | 0.2360 | 0.2802 | 0.2350 | 0.7805 | 0.2350 | 0.7579 | 0.7230 | 0.4392 |
| | Chromium | - | - | - | - | - | - | 0.0022 | 0.0014 |
| | Copper | 0.0055 | 0.0075 | 0.0020 | 0.0034 | 0.0020 | 0.0108 | 0.0033 | 0.0022 |
| | Iron | 0.0362 | 0.0241 | 0.0408 | 0.0034 | 0.0408 | 0.0066 | 0.0634 | 0.0559 |
| | Lithium | - | - | - | - | - | - | 0.0167 | 0.0152 |
| | Manganese | 0.0627 | 0.0578 | 0.0387 | 0.4285 | 0.0387 | 0.0547 | 0.0572 | 0.5567 |
| | Molybdenum | 0.0020 | 0.0025 | - | - | 0.0020 | 0.0048 | 0.0024 | 0.0054 |
| | Nickel | 0.0020 | 0.0052 | 0.0021 | 0.0094 | 0.0021 | 0.0081 | 0.0069 | 0.0036 |
| | Phosphorus | 4.7300 | 0.4173 | 2.7900 | 0.0555 | 2.7900 | 0.1023 | 5.5200 | 1.2654 |
| | Selenium | - | - | - | - | - | - | 0.0270 | 0.0166 |
| | Thallium | - | - | - | - | - | - | 0.0740 | 0.0145 |
| | Vanadium | 0.0010 | 0.0070 | 0.0010 | 0.0025 | 0.0010 | 0.0048 | 0.0055 | 0.0011 |
| | Zinc | 0.0350 | 0.0031 | 0.0027 | 0.0021 | 0.0027 | 0.0060 | 0.0049 | 0.0039 |

Note: red values represent higher outflow concentrations compared to inflow

Soil mixture inflow sample (C8) present a slight enrichment in certain metals when compared to other columns inflow concentrations, particularly in barium and boron. Besides that fact, when comparing inflow and outflow concentrations in the 11 parameters considered, Column 3 has 7 parameters where outflow concentration is higher than inflow, while Column 4 has 6 and Column 5 has 9. One keep in mind that Column 5 only has two outflow samples, which do not allow for a detailed overview of the general behaviour of the parameters considered. Column 8 has only 3 parameters in which outflow average concentration surpasses the inflow, suggesting an overall reduction of concentration in outflow besides the slight enrichment in inflow. Phosphorus shows the highest reduction in all columns. This is particularly useful taking into account that this element is very common in wastewater matrix.

Considering that boron is a rare element at soils, and it is usually retained by organic matter[5], boron concentration decrease in outflow may have resulted from increased presence of organic matter in the soil mixture. Zinc is heavily retained by clay minerals, hydrated metal oxides and organic matter (Alloway, 1990) being a good indicator of the

[5] http://www.soilandplantlaboratory.com/pdf/articles/BoronOverlookedEssential.pdf

effects of a possible increase of organic matter in soil mixture. It is also important to note that adsorption of Zn from soil solution by the solid soil particles is generally accompanied by simultaneous desorption of equivalent amounts of other cations from the solid phase to the soil solution.

Nitrogen cycle components overall results are presented in Table 33. Again, outflow (OUT) values represent the average of all outflow concentrations.

**Table 33 – Nitrogen components results comparison (mg/L)**

| | Parameter | Column 3 | | Column 4 | | Column 5 | | Column 8 | |
|---|---|---|---|---|---|---|---|---|---|
| | | IN | OUT | IN | OUT | IN | OUT | IN | OUT |
| Nitrogen cycle | Ammonia | 32.80 | 1.36 | 34.20 | 1.45 | 34.20 | 0.65 | 48.90 | 1.99 |
| | Nitrites | 0.02 | 1.10 | 0.005 | 5.08 | 0.005 | 3.51 | 0.01 | 2.10 |
| | Nitrates | 0.27 | 0.86 | 2.00 | 2.00 | 2.00 | 6.51 | 2.00 | 140.45 |

Note: red values represent higher outflow concentrations compared to inflow

The general behaviour is similar in natural soil and soil mixture, with high concentration of ammonia at inflow and a reduction at outflow. Both soil mixture and natural soil show similar results also in nitrites, with low concentration at inflow and high concentration at outflow average. This suggests a transformation of ammonia in nitrites and nitrites into nitrates. Excluding Column 4, the inflow of all columns has lower concentration of nitrates than outflow average. Although this may suggest that nitrites are being converted into nitrates, a careful investigation has to be taken considering the known problems with nitrates in SBM WWTP and the outflow average of Column 8. The first premise raises some doubts in nitrates values measured in the inflow, as nitrates always show very low values in comparison to background data in the study area. The second statement is related to the possible constitution of the organic soil used, as the main reason for such high concentration in nitrates in outflow water can result from a high concentration in the soil itself. This is not observed in the original soil. Besides this fact, similar behaviour with ammonia was observed by Ollivier *et al.* (2013) in a soil-column experiment, where $NH_4^+$ was the predominant form of nitrogen in the infiltrated treated wastewater but its concentration decreased sharply with depth, in which $NH_4^+$ is oxidized to $NO_3^-$ in aerated conditions. In the process $NH_4^+$ was retained in the uppermost soil layer and nitrification occurred in the top 1.5 m of soil.

Major ions results for all soil-column experiments are presented in Table 34. OUT refers to average of concentration per parameter at outflow sample.

**Table 34 – Major ions results comparison (mg/L)**

| | Parameter | Column 3 | | Column 4 | | Column 5 | | Column 8 | |
|---|---|---|---|---|---|---|---|---|---|
| | | IN | OUT | IN | OUT | IN | OUT | IN | OUT |
| Major ions | Calcium | 29.4 | 76.5 | 43.6 | 95.30 | 43.6 | 103.39 | 37.8 | 132.2 |
| | Chloride | - | 97.7 | 91.1 | 111.85 | 91.1 | 97.99 | 118 | 116.5 |
| | Magnesium | 17.4 | 31.0 | 29 | 47.80 | 29 | 45.80 | 28.4 | 40.6 |
| | Phosphate | 6.3 | 0.2 | 7.68 | 0.10 | 7.68 | 0.09 | 15.2 | 4.0 |
| | Potassium | 16.7 | 10.6 | 14.8 | 7.11 | 14.8 | 15.84 | 23.6 | 29.9 |
| | Sodium | 58.0 | 39.0 | 71.6 | 56.80 | 71.6 | 22.53 | 92.5 | 83.3 |
| | Sulphate | 88.0 | 8.9 | 64.7 | 82.45 | 64.7 | 52.63 | 70.9 | 77.3 |

Note: red values represent higher outflow concentrations compared to inflow

Overall behaviour is again similar in all columns, where a high concentration is measured at outflow for calcium, magnesium, potassium, sodium, and chloride. This suggest a and continuous washing out of the soil mineral matrix, with includes limestone, anorthite and montmorillonite (bentonite). These minerals are rich in Ca, Mg, K, Na. Similar behaviour was observed by Goren *et al.* (2011) where the recharge of secondary effluent into a calcareous sandstone aquifer was accompanied by $CaCO_3$ dissolution that increased the Ca concentration in the reclaimed water resulting in increasing water hardness.

High concentrations of chloride also suggest limestone reaction with acid solutions, although inflow concentration is not very different from outflow average. The main behaviour of this element is to be persistent.

Sulphate concentration decreases in Column 3 (from 88 mg/L at inflow to 8.9 mg/L at outflow) and in Column 5 (64.7 mg/L to 52.63 mg/L), while Column 4 and Column 8 show an increase at outflow. The difference in concentration reduction between C3 and C5 can be related to redox environment. C3 continuous inflow did not allow for the oxygenation of column, creating an oxygen depleted environment, allowing $SO_4^{2-}$ transformation. This is not the case in C5, where the saturation cycles allow for the oxygen presence in the column (at least in some sections). As Greskowiak *et al.* (2005) demonstrated in infiltration basins, the abrupt change from saturated to unsaturated conditions causes the most significant geochemical changes, including the rapid oxidation of sulphides accompanied by the dissolution of calcite.

Phosphate concentration is highly reduced throughout the experiments, but more in the natural soil.

The overall behaviour of Column 8 experiment concerning major ions is worse than that observed for natural soil column experiments. This may be the result of the addition of artificial sand, enriching the soil with limestone thus resulting in an increased leaching of major ions.

It is also important to note that this soil-column experienced a long period of non saturation (as discussed in Section 4.3.2.3.1) which resulted in a longer time of water-soil interaction and better oxygenation (with longer water residence due to the enhanced water retention capacity induced by OM) and therefore enhanced soil-water reactions, lowering pH in soil solution and increasing of desorption processes in metals. These were latter mobilized when outflow flux was re-established. This can provide significant information about the saturation/desaturation periods and their effects for basin functioning procedures.

If ELV values from Legislative Decreed 236/98 are used as reference and compared to average outflow values for each column (Table 35) it can be concluded that after soil-column filtration outflow concentrations are below limits defined by law. This means that limit values at discharge after treatment are respected. It’s important to refer that from the 26 parameters considered only six have emission limit values defined.

**Table 35 – Average outflow values vs ELV (Legislative decree 236/98)**

| | Parameter | Legislative decree 236/98 ELV (mg/L) | Column 3 | Column 4 | Column 5 | Column 8 |
|---|---|---|---|---|---|---|
| Metals | Aluminium | - | 0.0287 | 0.0110 | 0.0149 | 0.0179 |
| | Antimony | - | - | - | - | 0.0194 |
| | Barium | - | 0.2431 | 0.4855 | 0.4420 | 0.3753 |
| | Boron | - | 0.2802 | 0.7805 | 0.7579 | 0.4392 |
| | **Chromium** | **2** | - | - | - | **0.0014** |
| | **Copper** | **1** | **0.0075** | **0.0034** | **0.0108** | **0.0022** |
| | Iron | - | 0.0241 | 0.0034 | 0.0066 | 0.0559 |
| | Lithium | - | - | - | - | 0.0152 |
| | Manganese | - | 0.0578 | 0.4285 | 0.0547 | 0.5567 |
| | Molybdenum | - | 0.0025 | - | 0.0048 | 0.0054 |
| | **Nickel** | **2** | **0.0052** | **0.0094** | **0.0081** | **0.0036** |
| | **Phosphorus** | **10** | **0.4173** | **0.0555** | **0.1023** | **1.2654** |
| | Selenium | - | - | - | - | 0.0166 |
| | Thallium | - | - | - | - | 0.0145 |
| | Vanadium | - | 0.0070 | 0.0025 | 0.0048 | 0.0011 |
| | Zinc | - | 0.0031 | 0.0021 | 0.0060 | 0.0039 |
| Nitrogen cycle | Ammonia | - | 1.36 | 1.45 | 0.65 | 1.99 |
| | Nitrites | | 1.10 | 5.08 | 3.51 | 2.10 |
| | **Nitrates** | **50** | **0.86** | **2.00** | **6.51** | **140.45** |
| Major ions | Calcium | - | 76.5 | 95.30 | 103.39 | 132.2 |
| | Chloride | - | 97.7 | 111.85 | 97.99 | 116.5 |
| | Magnesium | - | 31.0 | 47.80 | 45.80 | 40.6 |
| | Phosphate | - | 0.2 | 0.10 | 0.09 | 4.0 |
| | Potassium | - | 10.6 | 7.11 | 15.84 | 29.9 |
| | Sodium | - | 39.0 | 56.80 | 22.53 | 83.3 |
| | **Sulphate** | **2000** | **8.9** | **82.45** | **52.63** | **77.3** |

In a more conservative approach using as reference the maximum recommended values for drinking water, a similar comparison to the average outflow concentration was made -Table 36. From the 26 parameters considered, fifteen of them have MRV defined by law. Aluminium, boron, nickel, chloride, sodium and sulphate concentrations at outflow are below MRV for all columns. On the other hand, manganese, ammonia and nitrites are above MRV in all columns, while nitrates are above MRV only in Column 8. Antimony and selenium were only determined for Column 8 outflow and are also above MRV.

These can be considered poor quality waters in terms of drinking water criteria, but one must keep in mind that this is treated wastewater not subjected to the same treatment as a drinking water. Also, soil-column experiments only show represent a small part of a SAT system, given that many processes of purification occur in larger depths of the aquifer.

**Table 36 - Average outflow values vs MRV (European Directive 98/83)**

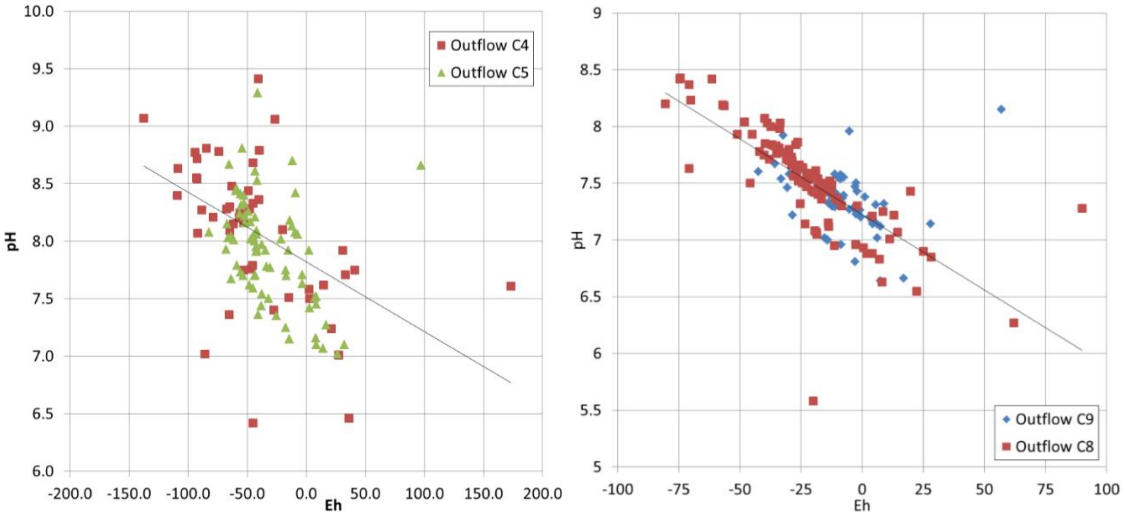
| | Parameter | European Directive 98/83 MRV (mg/L) | Column 3 | Column 4 | Column 5 | Column 8 |
|---|---|---|---|---|---|---|
| Metals | **Aluminium** | **0.2** | **0.0287** | **0.0110** | **0.0149** | **0.0179** |
| | **Antimony** | **0.005** | - | - | - | **0.0194** |
| | Barium | - | 0.2431 | 0.4855 | 0.4420 | 0.3753 |
| | **Boron** | **1** | **0.2802** | **0.7805** | **0.7579** | **0.4392** |
| | **Chromium** | **0.05** | - | - | - | **0.0014** |
| | **Copper** | **2** | **0.0075** | **0.0034** | **0.0108** | **0.0022** |
| | **Iron** | **0.2** | **0.0241** | **0.0034** | **0.0066** | **0.0559** |
| | Lithium | - | - | - | - | 0.0152 |
| | **Manganese** | **0.05** | **0.0578** | **0.4285** | **0.0547** | **0.5567** |
| | Molybdenum | - | 0.0025 | - | 0.0048 | 0.0054 |
| | **Nickel** | **0.02** | **0.0052** | **0.0094** | **0.0081** | **0.0036** |
| | Phosphorus | - | 0.4173 | 0.0555 | 0.1023 | 1.2654 |
| | **Selenium** | **0.01** | - | - | - | **0.0166** |
| | Thallium | - | - | - | - | 0.0145 |
| | Vanadium | - | 0.0070 | 0.0025 | 0.0048 | 0.0011 |
| | Zinc | - | 0.0031 | 0.0021 | 0.0060 | 0.0039 |
| Nitrogen cycle | **Ammonia** | **0.5** | **1.36** | **1.45** | **0.65** | **1.99** |
| | **Nitrites** | **0.5** | **1.10** | **5.08** | **3.51** | **2.10** |
| | **Nitrates** | **50** | **0.86** | **2.00** | **6.51** | **140.45** |
| Major ions | Calcium | - | 76.5 | 95.30 | 103.39 | 132.2 |
| | **Chloride** | **250** | **97.7** | **111.85** | **97.99** | **116.5** |
| | Magnesium | - | 31.0 | 47.80 | 45.80 | 40.6 |
| | Phosphate | - | 0.2 | 0.10 | 0.09 | 4.0 |
| | Potassium | - | 10.6 | 7.11 | 15.84 | 29.9 |
| | **Sodium** | **200** | **39.0** | **56.80** | **22.53** | **83.3** |
| | **Sulphate** | **250** | **8.9** | **82.45** | **52.63** | **77.3** |

In the pharmaceuticals analysis, Column 9 showed the best results, where none of the commonly persistent compounds were found in outflow, although atenolol, bisoprolol, metoprolol, propranolol, sotalol, diclofenac, gemfibrozil, naproxen and carbamazepine were detected in the inflow. In Column 3, outflow analysis showed carbamazepine, diclofenac, gemfibrozil, hydrochlorothiazide, ibuprofen, levetiracetam, naproxen and primidone above LOR. Column 4 showed bezafibrate, carbamazepine diclofenac, gemfibrozil and naproxen concentrations above LOR at outflow, while in Column 5 presented concentration above LOR of bezafibrate, carbamazepine diclofenac, gemfibrozil, ibuprofen and naproxen.

Concerning pH, Column 8 and Column 9 show slightly lower pH values at outflow in comparison with Column 3, 4 and 5. Eh values are very disperse with no direct relation with saturation/unsaturation cycles. Besides the high dispersion of these parameters,

there seems to be a negative correlation between both, with inverse relation (decrease of pH results in increase of Eh) - Graph 63.

This information may be useful for further experiments, both in laboratory scale and infiltration basin scale.




**Graph 63 – pH vs Eh for natural soil and soil mixture**

Batch experiment results for natural soil show similar results for soil-column experiments.

From the both batch experiments results comparison soil mixture shows better effects on supressing recalcitrant pharmaceuticals, where one out of 14 above LOR in inflow was detected in outflow, namely carbamazepine. This element also occurs in the outflow of the batch conducted in natural soil, where seven out of 14 above LOR show persistent behaviour.

Other parameters also show better results in soil mixture, where average of percentage of removal is 63.7% vs 56.9% of natural soil. Also, the number of compounds that showed concentration increase at outflow is higher in natural soil (13) than in soil mixture (9).

The increase of organic matter seems to have had a positive effect in terms of overall contaminant reduction. But the selected organic soil must be carefully chosen. In the selected soil mixture, there were unexpected results concerning nitrates. Higher concentrations at outflow can point to a possible contamination (accidental or intended addition) of these elements in the organic soil, since it is usually used as plants substrate. To control this, a careful analysis should be conducted if the organic soil is commercial, besides consulting the sellers' composition information. If possible this organic layer should be created in controlled conditions if time constraints allow it.

In a practical approach, considering an average volume discharged every day from wastewater treatment plant of 900 $m^3$/d (AdA and ERSAR, 2008), treated volume percentages can be calculated for the basins to be constructed based on the range of laboratory flow rates obtained. For the two basins programed to be constructed (each one with 15 m by 7 m = 105 $m^2$ area), a reactive layer of the natural soil, wastewater

volume that could be infiltrated ranges from 6 to 24 % of the total SB Messines WWTP outflow volume considering flow rates obtained at column scale for day 1 of experiment and without taking into account clogging effects - Table 37.

**Table 37 – Treated volumes for natural soil at basin scale**

| | Flow rate | | | | Treated % |
|---|---|---|---|---|---|
| | Column scale (A = 0.002 $m^2$) | | Basin scale (A = 210 $m^2$) | | |
| | ($cm^3$/min) | ($m^3$/d) | ($cm^3$/min) | ($m^3$/d) | |
| **Column 1** | 0.85 | 0.001 | 86967.99 | 125.23 | 13.91 |
| **Column 2** | 1.46 | 0.002 | 149778.20 | 215.68 | 23.96 |
| **Column 3** | 0.87 | 0.001 | 89332.37 | 128.64 | 14.29 |
| **Column 4** | 0.36 | 0.0005 | 37316.05 | 53.74 | 5.97 |
| **Column 5** | 1.50 | 0.002 | 154609.76 | 222.64 | 24.74 |

If characteristics determined for C8 and C9 (that shown better endurance to soil washing out processes and good long term behaviour) are considered, a reactive layer installed at the basin bottom can treat up to 71% of the considered average volume discharged daily in perfect conditions (i.e. no clogging effects) - Table 38. Again, flow rates considered correspond to 1 day of experiment in both columns. If flow rates for all the experiment time length (44 days) are considered the treated percentage decreases to 13% in Column 8 and 21% in Column 9.

**Table 38 – Treated volumes for soil mixture at basin scale**

| | Flow rate | | | | Treated % |
|---|---|---|---|---|---|
| | Column scale (A = 0.002 $m^2$) | | Basin scale (A = 210 $m^2$ each) | | |
| | ($cm^3$/min) | ($m^3$/d) | ($cm^3$/min) | ($m^3$/d) | |
| **Column 8** | 3.34 | 0.005 | 343348.80 | 494.42 | 54.94 |
| **Column 9** | 4.34 | 0.006 | 446250.63 | 642.60 | 71.40 |

## 6.1. Uncertainty associated with soil-column experiments

Uncertainty in the methodologies and procedures adopted can cause some lack of confidence in results, this is why for the sake of future research this must be described. A brief analysis of uncertainty must be conducted for the sole reason to understand the limitations of this type of experiments and also to keep track of the lacking information.

Effects of soil packing are somewhat dependent of, as previously seen, number of strikes (drops), but not only. The effect of weight dropping can change from user to user, and it's not possible to replicate with high confidence the same column. Even the dry filling procedure of the column, natural granulometric selection can occur and different interface can be created inside the soil column.

Concerning column assembling uncertainty factors a parallel benchmark was conducted in Column 8 and Column 9. The soil mixture that was used in the soil column had exactly the same composition. The same person conducted the filling and packing process in

both columns, following the exactly same steps. Pre-experiment saturation process was conducted in parallel and after experiment start the saturation cycles started at exactly the same time with the same water matrix being injected. Given those careful procedures to replicate every step in both columns the results were in fact different. Column 8 had a lower permeability than Column 9, and flow rates were repeatedly lower. After the experiment was discontinued, both soils where removed from the column and carefully observed. No evidences of preferential flow channels were observed.

Uncertainty in concentrations measured in column outflow samples or SBM WWTP effluent samples analysis for determination of pharmaceuticals concentration can be considered minor, since the values obtained are in the same interval scale, although conditions of sampling varied. Besides that fact, higher values at outflow than for inflow for pharmaceuticals were detected in column 3, 4 and 5. Both inflow and outflow sample conservation followed strict conservation rules, being kept in low temperatures previous to laboratory analysis.

The reasonable cause for this, and considering that there are no pharmaceutical compounds in the soil previous to the soil-column experiments, may be the fractioning process conducted in the inflow samples. After the SBM WWTP was collected in large container, it was divided into several smaller glass vials for both conservation and also for gradual infiltration in the column experiments. This fractioning process may have caused some kind of compound partition due to differentiated settling inside the main container before being divided into parts, thus having different concentrations in different bottles. The result may be that the outflow concentrations may not be representative of the values measured in one inflow analysis.

# 7. Synthesis, conclusions and recommendations

Soil-Aquifer Treatment (SAT) in Managed Aquifer Recharge (MAR) systems is a recharge option aiming to improve the quality of the recharged water while augmenting the water availability, helping to address water scarcity challenges.

In SAT-MAR basins, water percolates through the soil matrix under controlled conditions inducing water pre-treatment. In fact, as the effluent moves through the soil, natural soil filtration occurs and water undergoes significant quality improvements through physical, chemical and biological processes.

One of the main existing challenges of SAT-MAR is to control and maintain the infiltration rates and avoid clogging due to physical, chemical and biological processes taking place during the transport of water through the unsaturated and saturated zone. Soil-column experiments are frequently used to get information on the soil behaviour under controlled conditions.

In the framework of this dissertation carried out under EU MARSOL project (www.marsol.eu), several soil-column experiments were conducted at LNEC LASUB laboratory using a soil collected in SB Messines wastewater treatment plant, one of the Algarve demo sites. This dissertation presents the results obtained concerning the soil flow rate variations under different conditions, aiming at verifying the soil suitability for infiltration media in basins. It also presents the results for the improvement in water quality resulting from the soil capacity for sorption and biodegradation of the pollutants.

The laboratory experiments performed allowed gathering information on the short and long term behaviour, at laboratory scale, of São Bartolomeu de Messines natural soil and a soil mixture produced from it, providing the basis for deciding the best soil composition to be used in the SAT-MAR facility to be installed in SB Messines WWTP.

The first conclusion that can be drawn in that the soil collected in the outskirts of the SB Messines WWTP has shown some suitability to be used as a base infiltration layer for the SAT-MAR infiltration basins, in what concerns the infiltration capacity, but is expected to have some problems in the long term, with a continuous decrease in permeability. This has led to the need of a new soil composition mixture.

The production of a soil mixture composed of organic soil and “artificial sand” from crushed limestone mixed with natural SBM soil, resulted in a more pervious material with a good long term hydraulic behaviour, with better response to saturation/unsaturation cycles. Although organic matter percentage has increased the soil washout processes and compaction resulting from particle rearrangement, this was not very problematic for the permeability rates at long term.

Considering the average volume of 900 $m^3$/d discharged every day from wastewater treatment plant (AdA and ERSAR, 2008), the potential treated volume percentages were calculated for the basins to be constructed (each one with 15 m by 7 m = 105 $m^2$ area), based on the range of laboratory flow rates obtained.

For the two basins with a reactive layer of natural soil, the wastewater volume that could be infiltrated ranges from 6 – 24 % of the total SB Messines WWTP outflow volume,

considering the flow rates obtained at column scale for day 1 of experiment and without taking into account clogging effects (Table 37).

Considering the soil mixture (40% natural soil, 40% artificial sand and 20% organic soil), which has shown better endurance to soil washing out processes and good long term behaviour, a reactive layer installed at the basin bottom could treat up to 71% of the considered average volume discharged daily if no clogging effects are considered (Table 38). If flow rates measured at the end of experiment (44 days) are considered, treated percentage decreases to 21% of the daily discharged volume.

The removal of contaminants in the wastewater of SB Messines was analysed aiming to understand the best conditions for improving the water quality for the following main group of contaminants: metals, nitrogen cycle, pharmaceuticals and major ions.

Both natural soil and different soil mixtures were studied using cycles of saturation and non-saturation, the latter allowing the oxygenation of the soil column. The main conclusions that can be drawn are: (1) the presence of a soil mixture with an organic matter (OM) layer favours the retention/degradation (mainly through sorption and biotransformation processes) of most pharmaceuticals studied, as well as heavy metals (retained both in clay fraction and OM); (2) the sequence of oxic/anoxic conditions is the best approach to ensure maximum attenuation efficiency, since some elements degrade better in oxic conditions (for example for the biological oxidation of ammonia into nitrite, nitrate and nitrogen gas), and others are degraded under anaerobic conditions (example for several pharmaceuticals); and (3) the existence of high pH favours the retention of heavy metals attached to soils.

## 7.1. Recommendations

Given the results obtained, concerning both hydraulic and quality aspects, a set of considerations/recommendations can be made:

- The experimental results obtained in laboratory, both for permeability and recharge water quality, are different from basin scale experiments. This results from scaling factors as well as the natural soil heterogeneity, together with local differences resulting from changes in vegetation, topography or man activity.
- The exposure to field conditions that can vary widely, and are not possible to control as in soil-column experiments. At infiltration basin scale other processes, such as root growth in the reactive layer, could benefit the long-time hydraulic behaviour by smoothing the clogging effects, but on the other hand uncontrolled effluent (with the natural variations that a wastewater can experience) can have adverse results in the basin operational status.
- The increase in the organic matter content in the soil used for SAT-MAR has shown general improvement of the outflow water quality when compared with the inflow. Thus, if the natural soil to be used as reactive layer has low concentration of organic matter, it should be integrated in a soil mixture, *e.g*. in the form of humus or peat.
- The increase of organic matter can result in lowering the soil resistance, due to the increase in porosity resultant from the washing out processes; the latter

creates preferential flow paths, cavities and air pockets that led to the thickness decrease of the reactive layer. Consequently, the addition of a skeleton component can be useful to avoid these phenomena. “Artificial sand”, which is an inexpensive material produced from limestone crushing, was a good example to increase permeability and also to give structure to the soil, without any relevant impact in terms of quality at outflows as the matrix of this component is the same as the natural soil (limestone).

- The implementation of a procedure of saturation/unsaturation cycles allows the soil to oxygenate, enabling the degradation/retention of compounds under oxidation reactions, as well as periods of oxygen depleted environment that enhance anaerobic degradation. This will also reduce biological clogging effects, as the small turbulence of inflow water and air exposure can hinder biofilm production on the soil top.
- The implementation of too large periods (more than 1-2 days) of non-saturation conditions should be avoided to prevent drastic changes in pH and redox conditions which can result namely in the remobilization of metals (Graph 37,Graph 38,Graph 39 and Graph 52).
- The inflow water should be equally distributed along the reactive layer and water influx should be relatively low. This allows avoiding turbulence and the creation of suspended solids as well as the remobilization of contaminants retained in the soil matrix.
- Finally, although soil analysis results showed little to none concentration of pharmaceuticals retained in it, it’s expected that this reactive layer can have high contaminant concentration. Therefore, this reactive layer should be treated as a hazardous material, and if substitution is necessary due to maximum lifespan achievement, it should be collected, contained and afterwards destroyed to avoid additional pollution problems.

## 7.2. Research needs

Further studies will be conducted at the SAT-MAR basin scale that will help enriching the conclusions of this dissertation.

In terms of what was learned and considering the limitations of these experiments, several research needs are proposed:

- To confirm the presence of microorganisms capable of degrading pharmaceuticals in the column, particularly in the natural soil/soil mixture. These microorganisms with biodegradation potential can originate from the soil itself collected from the field site or injected with inflow water. This information would help understanding the degradation/transformation processes that occurred inside the columns.
- To monitor real time changes in parameters. This could help understanding the degradation processes and the importance of redox potential (Eh), total organic carbon (TOC), nutrients and pH, among others, in the chemical and biological processes occurring in the column. For example, the value in Eh and the consumption/production of oxidants can give insight into the types and extent of

biodegradation processes related with the decrease in pharmaceuticals concentration.

- To define the amount of organic matter needed to achieve good results. The addition of organic matter certainly had an effect in the retention of pharmaceuticals, but a larger number of soil-column experiments and batch experiments would be necessary to establish the most effective amount of OM to be added without compromising the reactive layer structure and retention capacity.
- To investigate other possible pre-existent contaminants in the organic soil to be mixed with original soil, aiming to prevent further contamination problems.
- To develop new soil-column and batch experiments using spiked concentrations (with known concentrations) of certain contaminants, allowing analysing the soil behaviour with water having higher concentrations than those used (but maintaining the same wastewater contaminants and emerging contaminants).

The knowledge achieved, particularly in quality of outflow aspects, may be of relevance to the legal framework, helping to establish reference values to the injection/infiltration water quality and suitable soils (and places) and materials to use in SAT-MAR processes, to produce successful results with minimum negative environmental impacts and an acceptable economic outcome.

# Bibliographic References


Abel, C. D. T. (2014) Soil Aquifer Treatment - Assessment and Applicability of Primary Effluent Reuse in Developing Countries. Submitted in fulfilment of the requirements of the Board for Doctorates of Delft University of Technology and of the Academic Board of the UNESCO-IHE Institute for Water Education for the Degree of Doctor. CRC Press/Balkema. 187pp.

Alloway, B. (1990) Heavy Metals in Soils. Wiley and Sons, 339pp.

Almeida, C., Mendes, J.L., Jesus, M.R., Gomes, A.J. (2000) Sistemas Aquíferos de Portugal Continental. Instituto da Água e Centro de Geologia da FCUL, 477-489p.

Appelo, C., Postma, D. (1996) Geochemistry, Groundwater and Pollution. A.A. Balkema publishers, 535p.

Arye, G., Dror, I., Berkowitz, B. (2011). Fate and transport of carbamazepine in soil aquifer treatment (SAT) infiltration basin soils. Chemosphere, 82(2), 244–252p.

Asano, T., Cotruvo, J. (2004) Groundwater recharge with reclaimed municipal wastewater: Health and regulatory considerations. Water Research, 38(8), 1941–1951p.

Barbosa, A.E. (1999) Highway Runoff Pollution and Design of Infiltration Ponds for Pollutant Retention in Semi-Arid Climates Ph.D. Dissertation, Environmental Engineering Laboratory, Aalborg University, 52pp.

Bekele, E., Toze, S., Patterson, B., Higginson, S. (2011). Managed aquifer recharge of treated wastewater: water quality changes resulting from infiltration through the vadose zone. Water Research, 45(17), 5764–5772p.

Benamar, A. (2013) Soil Clogging Phenomena in Vertical Flow. In Martin, R., (ed.) Clogging issues associated with MAR methods. AIH comission on MAR, Australia. 77-84p.

Bdour, A., Hamdi, M. and Tarawneh, Z. (2009). Perspectives on sustainable wastewater treatment technologies and reuse options in the urban areas of the Mediterranean region. Desalination, 237(1-3), 162-174pp.

Bouwer, H. (1991). Role of groundwater recharge in treatment and storage of wastewater for reuse. Water Science and Technology, 24(9), 295-302p.

Bouwer, H. (2000) Integrated water management: emerging issues and challenges. Agricultural Water Management Volume 45, Issue 3, 217–228p.

Bouwer, H. (2002) Artificial recharge of groundwaters: hydrogeology and engineering. Hydrogeology Journal 10. 121-142p.

Caballero, M.H. (2010) Soil Aquifer Treatment as a Pre-treatment for Organic Micropollutants Removal during Membrane Filtration. MSc Thesis- MWI-2010/05, 89pp.

Calisto V., Esteves V.I. (2009) Psychiatric pharmaceuticals in the environment. Chemosphere 77, 1257–1274p.

CEN/TS14405:2004 Technical Specification – Characterization of waste – Leaching behaviour tests – Up-flow percolation test (under specified conditions), European Committee for Standardization (2004) 25 pp.

Cha, W., Choi, H., Kim, J. and Kim, I. (2004). Evaluation of wastewater effluents for soil aquifer treatment in South Korea. Water Science and Technology, 50(2), 315-322p.

Christensen F.M. (1998) Pharmaceuticals in the Environment—A Human Risk? Regulatory Toxicology and Pharmacology 28, 212–221p.

Cunningham V.L., Binks S.P., Olson M.J. (2009) Human health risk assessment from the presence of human pharmaceuticals in the aquatic environment. Regulatory Toxicology and Pharmacology 53, 39–45p.

Deblonde, T., Cossu-Leguille, C., Hartemann, P. (2011) Emerging pollutants in wastewater: A review of the literature. International Journal of Hygiene and Environmental Health 214, 442-448p.

DEMEAU (2013) Decision trees for MAR impact evaluation, Identification of optimum conditions to face emerging pollutants removal in MAR systems. Deliverable 12.1. EU Grant Agreement no. 308339. 101pp.

DEMEAU (2015) Guidelining protocol for soil-column experiments assessing fate and transport of trace organics. Deliverable 12.3. EU Grant Agreement no. 308339. 54pp.

Diamantino, C. (2009) Recarga Artificial de Aquíferos. Aplicação ao Sistema Aquífero da Campina de Faro. Doutoramento em Geologia. Faculdade de Ciências da Universidade de Lisboa. 326pp.

Dillon, P., Pavelic, P., Page, D., Beringen, H., Ward, J. (2009) – Managed Aquifer Recharge, An Introduction. Waterlines. CSIRO, National Water Commission, 77pp.

DINA-MAR (2010) La Gestión de la Recarga Artificial de Acuiferos en el Marco del Desarrollo Sostenible – Desarrollo Tecnológico. Série Hidrologia Hoy 6. 494pp.

Domenico, P., Schwartz, F. (1998) Physical and Chemical Hydrogeology. Wiley, 506pp.

ENSAT (2012a) Enhancement of Soil Aquifer Treatment to Improve the Quality of Recharge Water in the Llobregat River Delta Aquifer. Technical Final Report. LIFE08 ENV/E/000117. 52pp.

ENSAT (2012b) Enhancement of Soil Aquifer Treatment to Improve the Quality of Recharge Water in the Llobregat River Delta Aquifer. Layman's Report. LIFE08 ENV/E/000117. 28pp.

EPA (1992) Batch-type Procedures for Estimating Soil Adsorption of Chemicals. 530-SW-87-006-F, United States Environmental Protection Agency, 116pp.

ERSAR (2008) Inventário Nacional de Sistemas de Abastecimento de Água e de Águas Residuais. Agência Portuguesa do Ambiente (http://insaar.apambiente.pt/index.php?id=11)

European Comission (2001) Artificial recharge of groundwater, Energy, Environment and Sustainable Development. EC project ENV4-CT95-0071. 342pp.

Gale, I. (ed.) (2005) Strategies for Managed Aquifer Recharge (MAR) in semi-arid areas. International Hydrological Programme (IHP), International Association of Hydrogeologists commission on Management of Aquifer Recharge IAH – MAR. 30pp.

Goren, O., Gavrieli, I., Burg, A., Lazar, B. (2011) Cation exchange and CaCO3 dissolution during artificial recharge of effluent to a calcareous sandstone aquifer. Journal of Hydrology, 400(1-2), 165–175p.

Greskowiak, J., Prommer, H., Massmann, G., Johnston, C., Nützmann, G., Pekdeger, A. (2005). The impact of variably saturated conditions on hydrogeochemical changes during artificial recharge of groundwater. Applied Geochemistry, 20(7), 1409–1426p.

Heberer, T. (2002) Tracking persistent pharmaceutical residues from municipal sewage to drinking water. Journal of Hydrology 266, 175-189p.

Heberer, T., Verstraeten, I., Meyer, M., Mechlinski, A., Reddersen, K. (2011) Occurrence and fate of pharmaceuticals during bank filtration – preliminary results from investigations in Germany and the United States. 14pp.

Henze, M., Comeau, Y. (2008) Biological Wastewater Treatment: Principles, Modelling and Design. IWA Publishing. 511pp.

Jacques, D., Šimůnek, J. (2005) User Manual of the Multicomponent Variably-Saturated Flow and Transport Model HP1, Description, Verification and Examples, Version 1.0, SCK/CEN-BLG-998, Waste and Disposal, SCK/CEN, 79 pp.

Jones O.A., Lester J.N., Voulvoulis N. (2005) Pharmaceuticals: a threat to drinking water? Trends in Biotechnology Vol.23 No.4, 163-167p.

Hillel, D. (1998) Environmental Soil Physics. Academic Press. 771pp.

Hutchison, A., Milczarek, M., Banerjee, M. (2013). Clogging Phenomena Related to Surface Water Recharge Facilities. In Martin, R., (ed.) Clogging issues associated with MAR methods. AIH comission on MAR, Australia. 84-95p.

Ilie, A.M. (2015) Personal communication.

Langmuir, D. (1997) Aqueous Environmental Geochemistry. Prentice Hall, 602pp.

Leitão, T.E., Zakharova, T.V. (2002) Risks of Contamination of Groundwater by Heavy Metals: Analysis of the Evolution of Contamination by Simulation in Laboratory Experiments. 2nd Phase Report. GIAS. LNEC, 47pp.

Leitão, T.E., Mota, R., Novo, M.E., Lobo-Ferreira, J.P. (2014) Combined Use of Electrical Resistivity Tomography and Hydrochemical Data to Assess Anthropogenic Impacts on

Water Quality of a Karstic Region: A Case Study from Querença-Silves, South Portugal. Journal of Environmental Processes, 15pp.

Lewis, J., Sjöstrom, J. (2010). Optimizing the experimental design of soil columns in saturated and unsaturated transport experiments. Journal of Contaminant Hydrology, 115(1-4), 1–13p.

LNEC (1966) Solos. Análise granulométrica. Série E196. Especificações LNEC, Documentação Normativa, 10pp.

LNEC (1993) Cimentos. Identificação dos constituintes cristalinos por difractometria dos raios X. Série E 403. Especificações LNEC, Documentação Normativa, 2pp.

Lobo Ferreira, J.P., Leitão, T.E., Oliveira, M.M., Novo, M.E., Monteiro, J.P., Salvador, N., Oliveira, L.G.S., Terceiro, P. Henriques, M.J., Martins, T., Mota, Lourenço, R., Machado, C., Pires, A., Almeida, A., Esteves, L., Rodrigues, L., Norberto, S., Tomé, M., Vilhena, J. (2013) PROWATERMAN – Água, Ecossistemas Aquáticos e Atividade Humana – Uma Abordagem Integrada e Participativa na Definição de Estratégias Inovadoras e Prospectivas de Gestão Integrada de Recursos Hídricos no Sul de Portugal. Projeto da Fundação para a Ciência e Tecnologia. Coordenado pelo Laboratório Nacional de Engenharia Civil. Livro final. 658pp.

Malolo, Y. (2011) Effect of Temperature and Redox Conditions on Removal of Contaminants during Soil Aquifer Treatment. UNESCO-IHE Institute for Water Education. MSc Thesis MWI-2011/09. 123p.

Mansell, J., Drewes, J. E., & Rauch, T. (2003). Removal mechanisms of endocrine disrupting compounds ( steroids ) during soil aquifer treatment. Water Science and Technology Vol 50 No 2, 229–237p.

MARSOL (2013) Demonstrating Managed Aquifer Recharge as a Solution to Water Scarcity andDrought. Document of Work. EU Grant agreement no: 619120. 43pp.

Martin, R., (ed.) (2013) Clogging issues associated with MAR methods. AIH comission on MAR, Australia. 213pp.

Miotliński, K., Barry, K., Dillon, P. (2010) Alice Springs SAT Project Hydrological and Water Quality Monitoring Report 2008-2009. CSIRO: Water for a Healthy Country National Research Flagship, 85p.

Monteiro, J.P., Guerreiro, P., Martins, J., Matos Silva, J., Reis, E. (2006) A Ribeira do Algibre e os Aquíferos do Algarve Central: Relações entre Águas Superficiais e Subterrâneas. Projecto POCI/AMB/57432/2004 Groundwater Flow Modelling and Optimisation of Groundwater Monitoring Networks at the Regional Scale in Coastal Aquifers: The Algarve Case Study.

Monteiro, J.P., Silva, J.M., Guerreiro, P., Martins, J., Reis, E. (2007) Modelação de Relações entre Águas Superficiais e Subterrâneas nos Aquíferos do Algarve Central. Seminário Sobre Águas Subterrâneas, Março 2007, APRH, Lisboa, 8pp.

Murray, R., Gideon, T., Revenscroft, P., Botha, F. (2007) Artificial Recharge Strategy: Version 1.3. Department of Water Affair and Forestry, Water Research Commission. 194pp.

Murray, R., Revenscroft, P. (2010) Potential Artificial Recharge Schemes: Planning for Implementation. Department of Water Affairs, 137pp.

National Research Council (1994) Ground Water Recharge Using Waters of Impaired Quality, National Academy Press. Washington D.C., 282pp.

Oliveira M.M. (2011) Conceptualization of recharge processes and water budgets of aquifer systems in watershed's water resources management framework. 8th Seminar on Groundwater, 15pp.

Oliveira M.M., Oliveira L, Lobo Ferreira JP (2008) Evaluation of natural recharge of Querença-Silves aquifer system (Algarve). 9th Water Congress, Cascais, 15 pp.

Ollivier, P., Surdyk, N., Azaroual, M., Besnard, K., Casanova, J., Rampnoux, N. (2013) Linking water quality changes to geochemical processes occurring in a reactive soil column during treated wastewater infiltration using a large-scale pilot experiment: Insights into Mn behavior. Chemical Geology, 356, 109–125p.

Parkhurst D.L., and Appelo C.A.J (2013) Description of input and examples for PHREEQC version 3—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey Techniques and Methods, 497pp.

Pavelic, P., Dillon, P., Mucha, M., Nakai, T., Barry, K., Bestland, E. (2011). Laboratory assessment of factors affecting soil clogging of soil aquifer treatment systems. Water Research, 45(10), 3153–3163p.

Pintor, A., Ferreira, C., Pereira, J., Correia, P., Silva, S., Vilar, V., Botelho, C., Boaventura, R. (2012). Use of cork powder and granules for the adsorption of pollutants: a review. Water Research, 46(10), 3152–66p.

Ramos, C., Carbonell, E. (1991) Nitrate leaching and soil moisture prediction with the LEACHM model. Fertilizer Research 27, 171-180p.

Reis, E., Gago, C., Borges, G., Matos, M., Cláudio, A., Mendes, E., Silva, A., Serafim, J., Rodrigues, A., Correia, S. (2007) Contribuição para o Cálculo do Balanço Hídrico dos Principais Sistemas Aquíferos do Algarve. Ministério do Ambiente, do Ordenamento do Território e do Desenvolvimento Regional. Comissão de Coordenação e Desenvolvimento Regional, 41pp.

Richardson, M., Bowron, J. (1985) The fate of pharmaceutical chemicals in the aquatic environment. Journal of Pharmacy and Parmacology 37, 12pp.

Schwab, B., Hayes, E., Fiori, J., Mastrocco, F., Roden, N., Cragin, D., Meyerhoff, R., D'Aco, V., Anderson, P. (2005) Human pharmaceuticals in US surface waters A human health risk assessment. Regulatory Toxicology and Pharmacology 42, 296-312p.

Šimůnek, J., Šejna, M., Saito, H., Sakai, M., van Genuchten, M. (2013) The HYDRUS 1.D Software Package for Simulating the One-Dimentional Movement of Water, Heat, and Multiple Solutes in Variably-Saturated Media – Version 4.17. Department of Environmental Sciences, University of California, 308pp.

Strathmann, T., Hu, L., Martin, H. (2010) Oxidation of Pharmaceutically Active Compounds During Water Treatment. Project 4066. 4pp.

Teijon, G., Candela, L., Tamoh, K., Molina-Díaz, A., Fernández-Alba, R. (2010) Occurrence of emerging contaminants, priority substances (2008/105/CE) and heavy metals in treated wastewater and groundwater at Depurbaix facility (Barcelona, Spain). The Science of the Total Environment, 408(17), 3584–3595p.

Ternes, T. (1998) Occurrence of drugs in german sewage treatment plants and rivers. Water Resources 32, 3245-3260p.

Mes, T. De, Zeeman, G., Lettinga, G. (2005) Occurrence and fate of estrone , 17 b - estradiol and 17 a -ethynylestradiol in STPs for domestic wastewater, Reviews in Environmental Science and Bio/Technology, 275–311p.

Ying, G., Kookana, R., Dillon, P. (2004) Attenuation of Two Estrogen Compounds in Aquifer Materials Supplemented with Sewage Effluent. Ground Water Monitoring & Remediation, 24(2), 102–107p.

Walczack, R., Rovdan, R., Witkowska-Walczak, B. (2002) Water retention characteristics of peat and sand mixtures. International Agrophysics 161, Institute of Agrophysics, Polish Academy of Sciences, 5pp.

Webb, S., Ternes, T., Gibert, M., Olejniczak, K. (2003) Indirect human exposure to pharmaceuticals via drinking water. Toxicology Letters 142, 157-167p.

# Appendix section

# Appendix 1 – São Bartolomeu de Messines WWTP effluent monitoring data

**Table 39 – SBM WWTP effluent monitoring results (AdA, 2009 – 2014)**

| Date | pH | BOD (mg/L) | COD (mg/L) | P total (mg/L) | N total (mg/L) | TSS (mg/L) | Cl (mg/L) | Total Coliforms |
|---|---|---|---|---|---|---|---|---|
| jan-09 | 7.7 | 10 | 40 | - | - | - | - | 2400 |
| fev-09 | 7.7 | 29 | 72 | 4.4 | 31 | 94 | 112 | 240000 |
| mar-09 | 7.8 | 34 | 119 | 4.8 | 38 | 65 | 119 | 540000 |
| abr-09 | 7.7 | 21 | 67 | - | - | - | - | 1500 |
| mai-09 | 7.8 | 54 | 176 | 5.9 | 41 | 57 | 170 | 22000 |
| jun-09 | 8 | 34 | 208 | 6.3 | 37 | 71 | 159 | 30000 |
| jul-09 | 8.8 | 52 | 196 | 6.5 | 33 | 89 | 170 | 23000 |
| ago-09 | 7.8 | 42 | 214 | 7.2 | 44 | 141 | | 21000 |
| set-09 | 8.1 | 89 | 288 | 8.2 | 48 | 161 | 164 | 100000 |
| out-09 | 8.1 | 36 | 165 | 5.7 | 34 | 45 | 145 | 160000 |
| nov-09 | 7.9 | 41 | 180 | 5.9 | 43 | 72 | 135 | 160000 |
| dez-09 | 7.6 | 40 | 131 | 5.1 | 43 | 59 | 131 | 265000 |
| jan-10 | 8.2 | 11 | 41 | 1.9 | 13 | 32 | 67 | 20000 |
| fev-10 | 8.6 | 20 | 82 | 5.3 | 24 | 148 | 80 | 30000 |
| mar-10 | 8.9 | 7 | 37 | 2.7 | 13 | 79 | 62 | 5000 |
| abr-10 | 8.6 | 16 | 96 | 3.9 | 21 | 91 | 92 | 727 |
| mai-10 | 8 | 26 | 108 | 4.5 | 30 | 113 | 103 | 58000 |
| jun-10 | 7.7 | 26 | 172 | 5.8 | 31 | 49 | 110 | 4400 |
| jul-10 | 8.6 | 70 | 248 | 6.6 | 41 | 119 | 118 | 23000 |
| set-10 | 8 | 33 | 210 | 6.5 | 41 | 110 | 121 | 28000 |
| out-10 | 8.1 | 37 | 206 | 6 | 38 | 76 | 121 | 70000 |
| nov-10 | 7.7 | 50 | 150 | 6 | 46 | 80 | 117 | 400000 |
| dez-10 | 7.5 | 25 | 75 | 4.1 | 33 | 83 | 92 | 460000 |
| jan-11 | 7.7 | 15 | 59 | 2.6 | 22 | 60 | 77 | 3180 |
| fev-11 | 8.3 | 10 | 63 | 3.1 | 26 | 87 | 97 | 54700 |
| mar-11 | 7.7 | 19 | 83 | 3.9 | 28 | 91 | 88 | 34500 |
| abr-11 | 8.6 | 39 | 119 | 4.1 | 20 | 62 | 109 | 17200 |
| mai-11 | 8.6 | 17 | 107 | 32 | 21 | 45 | 92 | 42600 |
| jun-11 | 7.7 | 27 | 125 | 5 | 33 | 56 | 111 | 12000 |
| set-11 | 7.6 | 55 | 214 | 6.3 | 37 | 78 | 128 | 155000 |
| nov-11 | 7.8 | 17 | 100 | 4.5 | 28 | 63 | 99 | 68700 |
| dez-11 | 7.6 | 15 | 81 | 3.2 | 23 | 61 | 98 | 4350 |
| jan-12 | 7.9 | 14 | 80 | 4.3 | 41 | 73 | 116 | 969 |
| fev-12 | 7.7 | 28 | 97 | 4.8 | 45 | 79 | 119 | 4350 |
| mar-12 | 7.7 | 8 | 71 | 6.7 | 53 | 100 | 121 | 10000 |
| abr-12 | 7.7 | 11 | 52 | 5.9 | 39 | 38 | 119 | 135000 |

| Date | pH | BOD (mg/L) | COD (mg/L) | P total (mg/L) | N total (mg/L) | TSS (mg/L) | Cl (mg/L) | Total Coliforms |
|---|---|---|---|---|---|---|---|---|
| mai-12 | 7.9 | 18 | 107 | 5.5 | 33 | 86 | 124 | 200 |
| jul-12 | 7.6 | 40 | 140 | 7 | 36 | 210 | 170 | 11000 |
| set-12 | 7.6 | 200 | 400 | 5.9 | 46 | 180 | 157 | - |
| nov-12 | 7.7 | 13 | 45 | 5.7 | 39 | 110 | 110 | 130000 |
| dez-12 | 8 | <10 | 44 | 3.5 | 26 | 75 | 107 | 25 |
| jan-13 | 7.7 | 13 | 41 | 4.3 | 31 | 68 | 93 | 8700 |
| fev-13 | 7.6 | 220 | 360 | 5.6 | 46 | 140 | 87 | - |
| mar-13 | 7.9 | <10 | 37 | 2.6 | 22 | 66 | 77 | 28 |
| abr-13 | 8.3 | <10 | 30 | 2.3 | 19 | 55 | 82 | 130 |
| mai-13 | 8.2 | 14 | 47 | 4.3 | 27 | 100 | 91 | 5800 |
| jun-13 | 8.7 | <10 | 58 | 4.4 | 27 | 100 | 105 | 2900 |
| jul-13 | 8.4 | <10 | 80 | 4.6 | 21 | 44 | 220 | 300 |
| ago-13 | 7.7 | 11 | 63 | 6.5 | 31 | 150 | 96 | 1700 |
| set-13 | 8.1 | 18 | 70 | 5.3 | 24 | 60 | 98 | 8 |
| out-13 | 7.9 | 12 | 34 | 5.2 | 30 | 130 | 92 | 690 |
| nov-13 | 8.7 | 6 | 45 | 3.8 | 32 | 120 | 80 | 30 |
| dez-13 | 7.6 | <10 | 35 | 4.1 | 35 | 54 | 89 | 580 |
| jan-14 | 7.6 | 10 | 37 | 4.3 | 31 | 80 | 89 | 2600 |
| fev-14 | 7.8 | <10 | 33 | 3.8 | 30 | 80 | 89 | 210 |
| ago-14 | 7.4 | 18 | 70 | 7 | 30 | 110 | 106 | 1600 |

# Appendix 2 – São Bartolomeu de Messines WWTP campaign measured pharmaceuticals

**Table 40 - SBM WWTP effluent campaign results (NA – not analysed)**

| Parameter | Unit | May 2014 | September 2014 |
|---|---|---|---|
| 16a-Hydroxyestron | µg/L | NA | <0.01 |
| 17a-Ethinylestradiol | µg/L | NA | <0.01 |
| 2,2´,4,4´,6,6´-Hexabromo-biPh | µg/L | NA | <0.01 |
| 2,2´,4,5,5´-Pentabromo-biPh | µg/L | NA | <0.01 |
| 2,2´,4´,5-Tetrabromo-biPh | µg/L | NA | <0.01 |
| 2,3´,5-Tribromo-biPh | µg/L | NA | <0.01 |
| 2,4-Dibromo-biPh | µg/L | NA | <0.01 |
| 2-Bromo-biPh | µg/L | NA | <0.01 |
| 4-Nonylphenol, Isomerengemisch | µg/L | NA | <0.02 |
| **4-tert.-Octylphenol** | **µg/L** | NA | **0.04** |
| **Acesulfam** | **µg/L** | NA | **18.3** |
| Acetylsalicylsäure | µg/L | NA | <0.02 |
| aminopyrin | µg/L | <0.05 | NA |
| **Amidotrizoesäure** | **µg/L** | NA | **0.52** |
| **Atenolol** | **µg/L** | NA | **0.09** |
| Atrazin | µg/L | NA | <0.01 |
| BDE 100 | µg/L | NA | <0.005 |
| BDE 153 | µg/L | NA | <0.005 |
| BDE 183 | µg/L | NA | <0.005 |
| BDE 28 | µg/L | NA | <0.005 |
| BDE 47 | µg/L | NA | <0.005 |
| BDE 77 | µg/L | NA | <0.005 |
| BDE 99 | µg/L | NA | <0.005 |
| BDE154 | µg/L | NA | <0.005 |
| BDE-Summe | µg/L | NA | <0.005 |
| **beta-Sitosterol** | **µg/L** | NA | **10.6** |
| Betaxolol | µg/L | NA | <0.01 |
| Bezafibrat | µg/L | NA | <0.01 |
| **Bisoprolol** | **µg/L** | NA | **0.04** |
| **Bisphenol A** | **µg/L** | NA | **0.09** |
| **Carbamazepin** | **µg/L** | **0.33** | **0.51** |
| cyklofosfamid | µg/L | <0.01 | NA |
| Chloramphenicol | µg/L | NA | <0.01 |
| Chlortetracyclin | µg/L | NA | <0.05 |
| Clarithromycin | µg/L | NA | <0.05 |
| Clofibrinsäure | µg/L | <0.02 | <0.02 |
| **Caffeine** | **µg/L** | **0.14** | **0.1** |
| Cyclamat | µg/L | NA | <0.05 |
| dapson | µg/L | <0.05 | NA |
| **DEET** | **µg/L** | NA | **0.08** |

| Parameter | Unit | May 2014 | September 2014 |
|---|---|---|---|
| Dehydrato-Erythromycin | µg/L | NA | <0.06 |
| Diazepam | µg/L | NA | <0.01 |
| **Diclofenac** | **µg/L** | NA | **0.24** |
| Doxicyclin | µg/L | NA | <0.05 |
| **EDTA** | **µg/L** | NA | **6.6** |
| Erythromycin | µg/L | <0.01 | <0.06 |
| Estradiol | µg/L | NA | <0.01 |
| Estriol | µg/L | NA | <0.01 |
| Estron | µg/L | NA | <0.01 |
| etinylöstradiol EE2 | µg/L | <0.50 | NA |
| Etofibrat | µg/L | NA | <0.02 |
| fenazon | µg/L | <0.01 | NA |
| Fenofibrat | µg/L | <0.01 | <0.04 |
| Fenoprofen | µg/L | NA | <0.02 |
| fenoterol | ng/l | <0.02 | NA |
| Gemfibrozil | µg/L | NA | <0.02 |
| Hexachlorbutadien (HCBd) | µg/L | NA | <0.01 |
| Ibuprofen | µg/L | NA | <0.01 |
| Indometacin | µg/L | NA | <0.02 |
| Iodipamid | µg/L | NA | <0.01 |
| Iohexol | µg/L | NA | <0.01 |
| **Iomeprol** | **µg/L** | NA | **0.07** |
| Iopamidol | µg/L | NA | <0.01 |
| **Iopromid** | **µg/L** | NA | **7** |
| Iothalamicsäure | µg/L | NA | <0.01 |
| Ioxaglinsäure | µg/L | NA | <0.01 |
| **Ioxithalaminsäure** | **µg/L** | NA | **0.06** |
| lincomycin | µg/L | <0.01 | NA |
| Ketoprofen | µg/L | NA | <0.01 |
| Mestranol | µg/L | NA | <0.01 |
| **Metoprolol** | **µg/L** | <0.06 | **0.04** |
| monensin | µg/L | <0.01 | NA |
| **Naproxen** | **µg/L** | NA | **0.4** |
| oleandomycin | µg/L | <0.02 | NA |
| östron | ng/l | <0.10 | NA |
| Oxytetracyclin | µg/L | NA | <0.05 |
| Parathion-methyl | µg/L | NA | <0.02 |
| Pentoxifyllin | µg/L | <0.01 | <0.01 |
| Phenacetin | µg/L | NA | <0.01 |
| Phenazon | µg/L | NA | <0.01 |
| Pindolol | µg/L | NA | <0.01 |
| primidon | µg/L | <0.04 | NA |
| progesteron | µg/L | <0.01 | NA |
| **Propanolol** | **µg/L** | <0.01 | **0.03** |
| Roxithromycin | µg/L | <0.01 | <0.02 |
| Saccharin | µg/L | NA | <0.05 |

| Parameter | Unit | May 2014 | September 2014 |
|---|---|---|---|
| Saccharin | µg/L | NA | NA |
| **Sotalol** | **µg/L** | NA | **0.07** |
| spiramycin | µg/L | <0.05 | NA |
| sulfadimidin | µg/L | <0.05 | NA |
| Sulfadiazin | µg/L | NA | <0.01 |
| Sulfadimidin | µg/L | NA | <0.01 |
| **Sulfamethoxazol** | **µg/L** | NA | **0.02** |
| Tetracyclin | µg/L | NA | <0.05 |
| tiamulin | µg/L | <0.01 | NA |
| TMDD | µg/L | NA | <0.02 |
| **Trimethoprim** | **µg/L** | <0.02 | **0.01** |
| **Tris(1,3-dichlor-2-propyl)phosphat** | **µg/L** | NA | **0.5** |
| Tris(1,3-dichlor-2-propyl)phosphat | µg/L | NA | NA |
| **Tris(1-chlor-2-propyl)phosphat** | **µg/L** | NA | **1.5** |
| Tris(1-chlor-2-propyl)phosphat | µg/L | NA | NA |
| **Tris(2-chloroethyl)phosphat** | **µg/L** | NA | **0.52** |
| Tris(2-chloroethyl)phosphat | µg/L | NA | NA |

# Appendix 3 – Column 3 soil analysis results

**Table 41 – Column 3 soil analysis extended results**

| Parameter | Unit | LOR | Sample 1 (top section) | Section 2 (bottom section) |
|---|---|---|---|---|
| Boron | mg/kg DW | 1.0 | 13.4 | 15.4 |
| Copper | mg/kg DW | 1.0 | 32.2 | 33.3 |
| Zinc | mg/kg DW | 3.0 | 30.4 | 31.2 |
| Ammonia | mg/kg DW | 0.50 | 60.3 | 19.8 |
| Nitrates | mg/kg DW | 20 | <20 | <20 |
| Nitrites | mg/kg DW | 0.050 | 0.248 | 0.238 |
| Phosphorus | % DW | 0.050 | 0.267 | 0.235 |
| Phosphates | % DW | 0.10 | 0.61 | 0.54 |
| Sulphate | % DW | 0.10 | 0.12 | <0.1 |
| Dry matter @ 105°C | % | 0.10 | 73.20% | 74.70% |
| Bezafibrate | mg/kg dw | 0.02 | <0.02 | |
| Chloramphenicol | mg/kg dw | 0.02 | <0.02 | |
| Clofibrineacid | mg/kg dw | 0.02 | <0.02 | |
| Cloxacilline | mg/kg dw | 0.02 | <0.02 | |
| Diclofenac | mg/kg dw | 0.02 | <0.02 | |
| Dicloxacilline | mg/kg dw | 0.02 | <0.02 | |
| Fenoprofen | mg/kg dw | 0.02 | <0.02 | |
| Gemfibrozil | mg/kg dw | 0.02 | <0.02 | |
| Ibuprofen | mg/kg dw | 0.02 | <0.02 | |
| Indomethacine | mg/kg dw | 0.04 | <0.04 | |
| Ketoprofen | mg/kg dw | 0.02 | <0.02 | |
| Nafcilline | mg/kg dw | 0.02 | <0.02 | |
| Naproxen | mg/kg dw | 0.04 | <0.04 | |
| Oxacilline | mg/kg dw | 0.02 | <0.02 | |
| Sulfamethoxazole | mg/kg dw | 0.02 | <0.02 | |
| Tolfenaminoacid | mg/kg dw | 0.02 | <0.02 | |
| Benzocaine | mg/kg ds | 0.01 | <0.01 | |
| Bezafibrate | mg/kg ds | 0.01 | <0.01 | |
| Carbamazepine | mg/kg ds | 0.01 | <0.01 | |
| Chloramphenicol | mg/kg ds | 0.01 | <0.01 | |
| Clindamycin | mg/kg ds | 0.01 | <0.01 | |
| Cloxacillin | mg/kg ds | 0.01 | <0.01 | |
| Clozapine | mg/kg ds | 0.01 | <0.01 | |
| Cortisone | mg/kg ds | 0.01 | <0.01 | |
| Cyclophosphamide | mg/kg ds | 0.01 | <0.01 | |
| Dapsone | mg/kg ds | 0.01 | <0.01 | |
| Dexamethasone | mg/kg ds | 0.01 | <0.01 | |
| Diazepam | mg/kg ds | 0.01 | <0.01 | |
| Diclofenac | mg/kg ds | 0.01 | <0.01 | |
| Dicloxacillin | mg/kg ds | 0.01 | <0.01 | |
| Dipyridamole | mg/kg ds | 0.01 | <0.01 | |
| Fenofibrate | mg/kg ds | 0.01 | <0.01 | |

| Parameter | Unit | LOR | Sample 1 (top section) | Section 2 (bottom section) |
|---|---|---|---|---|
| Fenoprofen | mg/kg ds | 0.01 | <0.01 | |
| Fenoterol | mg/kg ds | 0.01 | <0.01 | |
| Florfenicol | mg/kg ds | 0.01 | <0.01 | |
| Furazolidone | mg/kg ds | 0.01 | <0.01 | |
| Gemfibrozil | mg/kg ds | 0.01 | <0.01 | |
| Ifosfamide | mg/kg ds | 0.01 | <0.01 | |
| Indometacin | mg/kg ds | 0.01 | <0.01 | |
| Irbesartan | mg/kg ds | 0.01 | <0.01 | |
| Ketoprofen | mg/kg ds | 0.01 | <0.01 | |
| Levetiracetam | mg/kg ds | 0.01 | <0.01 | |
| Lidocaine | mg/kg ds | 0.01 | <0.01 | |
| Lincomycin | mg/kg ds | 0.01 | <0.01 | |
| Mebendazole | mg/kg ds | 0.01 | <0.01 | |
| Metronidazole | mg/kg ds | 0.01 | <0.01 | |
| Monensin | mg/kg ds | 0.01 | <0.01 | |
| Naficillin | mg/kg ds | 0.01 | <0.01 | |
| Oxacillin | mg/kg ds | 0.01 | <0.01 | |
| Oxazepam | mg/kg ds | 0.01 | <0.01 | |
| Pentoxifylline | mg/kg ds | 0.01 | <0.01 | |
| Phenazone | mg/kg ds | 0.01 | <0.01 | |
| Primidone | mg/kg ds | 0.01 | <0.01 | |
| Progesterone | mg/kg ds | 0.01 | <0.01 | |
| Propranolol | mg/kg ds | 0.01 | <0.01 | |
| Quetiapine | mg/kg ds | 0.01 | <0.01 | |
| Ronidazole | mg/kg ds | 0.01 | <0.01 | |
| Sulfachloropyridazine | mg/kg ds | 0.01 | <0.01 | |
| Sulfadimethoxine | mg/kg ds | 0.01 | <0.01 | |
| Sulfadimidine | mg/kg ds | 0.01 | <0.01 | |
| Sulfamerazine | mg/kg ds | 0.01 | <0.01 | |
| Sulfamethoxazole | mg/kg ds | 0.01 | <0.01 | |
| Sulfaquinoxaline | mg/kg ds | 0.01 | <0.01 | |
| Tiamulin | mg/kg ds | 0.01 | <0.01 | |
| Triclocarban | mg/kg ds | 0.01 | <0.01 | |
| Trimethoprim | mg/kg ds | 0.01 | <0.01 | |
| Tylosin | mg/kg ds | 0.01 | <0.01 | |
| Warfarin | mg/kg ds | 0.01 | <0.01 | |
| 4-Dimethylaminoantipyrine | mg/kg ds | 0.01 | <0.01 | |

# Appendix 4 – Column 5 soil analysis results

**Table 42 – Column 5 soil analysis extended results**

| Parameter | Unit | LOR | Sample 1 (top section) | Section 2 (bottom section) |
|---|---|---|---|---|
| Boron | mg/kg DW | 1.0 | 11.8 | 9.2 |
| Copper | mg/kg DW | 1.0 | 30.1 | 34.3 |
| Zinc | mg/kg DW | 3.0 | 27.4 | 48 |
| Ammonia | mg/kg DW | 0.50 | 71.2 | 17.6 |
| Nitrates | mg/kg DW | 20 | 140 | 25 |
| Nitrites | mg/kg DW | 0.050 | 184 | 7.98 |
| Phosphorus | % DW | 0.050 | 0.124 | 0.105 |
| Phosphates | % DW | 0.10 | 0.28 | 0.24 |
| Sulphate | % DW | 0.10 | <0.1 | <0.1 |
| Dry matter @ 105°C | % | 0.10 | 77.50% | 76.40% |
| Bezafibrate | mg/kg dw | 0.01 | <0.01 | <0.01 |
| Chloramphenicol | mg/kg dw | 0.01 | <0.01 | <0.01 |
| Clofibrineacid | mg/kg dw | 0.01 | <0.01 | <0.01 |
| Cloxacilline | mg/kg dw | 0.01 | <0.01 | <0.01 |
| Diclofenac | mg/kg dw | 0.01 | <0.01 | <0.01 |
| Dicloxacilline | mg/kg dw | 0.01 | <0.01 | <0.01 |
| Fenoprofen | mg/kg dw | 0.01 | <0.01 | <0.01 |
| Gemfibrozil | mg/kg dw | 0.01 | <0.01 | <0.01 |
| Ibuprofen | mg/kg dw | 0.01 | <0.01 | <0.01 |
| Indomethacine | mg/kg dw | 0.02 | <0.02 | <0.02 |
| Ketoprofen | mg/kg dw | 0.01 | <0.01 | <0.01 |
| Nafcilline | mg/kg dw | 0.01 | <0.01 | <0.01 |
| Naproxen | mg/kg dw | 0.02 | <0.02 | <0.02 |
| Oxacilline | mg/kg dw | 0.01 | <0.01 | <0.01 |
| Sulfamethoxazole | mg/kg dw | 0.01 | <0.01 | <0.01 |
| Tolfenaminoacid | mg/kg dw | 0.01 | <0.01 | <0.01 |
| Benzocaine | µg/kg dw | 5 | <5 | <5 |
| Caffeine | µg/kg dw | 5 | 57 | 5.3 |
| Carbadox | µg/kg dw | 25 | <25 | <25 |
| Carbamazepine | µg/kg dw | 5 | <5 | <5 |
| Clindamycin | µg/kg dw | 5 | <5 | <5 |
| Clozapine | µg/kg dw | 5 | <5 | <5 |
| Cortisone | µg/kg dw | 10 | <10 | <10 |
| Cyclophosphamide | µg/kg dw | 5 | <5 | <5 |
| Dapsone | µg/kg dw | 5 | <5 | <5 |
| Dexamethasone | µg/kg dw | 5 | <5 | <5 |
| Diazepam | µg/kg dw | 5 | <5 | <5 |
| Dimetridazole | µg/kg dw | 5 | <5 | <5 |
| Dipyridamole | µg/kg dw | 5 | <5 | <5 |
| Etoposide | µg/kg dw | 10 | <10 | <10 |
| Fenofibrate | µg/kg dw | 5 | <5 | <5 |
| Fenoterol | µg/kg dw | 5 | <5 | <5 |
| Florfenicol | µg/kg dw | 5 | <5 | <5 |
| Fluoxetine | µg/kg dw | 5 | <5 | <5 |
| Furazolidone | µg/kg dw | 25 | <25 | <25 |

| Parameter | Unit | LOR | Sample 1 (top section) | Section 2 (bottom section) |
|---|---|---|---|---|
| Gemcitabine | µg/kg dw | 5 | <5 | <5 |
| Ifosfamide | µg/kg dw | 5 | <5 | <5 |
| Irbesartan | µg/kg dw | 5 | <5 | <5 |
| Levetiracetam | µg/kg dw | 5 | <5 | <5 |
| Lidocaine | µg/kg dw | 5 | <5 | <5 |
| Lincomycin | µg/kg dw | 5 | <5 | <5 |
| Mebendazole | µg/kg dw | 5 | <5 | <5 |
| Metoprolol | µg/kg dw | 5 | <5 | <5 |
| Metronidazole | µg/kg dw | 5 | <5 | <5 |
| Monensin | µg/kg dw | 5 | <5 | <5 |
| Oxazepam | µg/kg dw | 5 | <5 | <5 |
| Paracetamol (acetaminophen) | µg/kg dw | 5 | <5 | <5 |
| Pentoxifylline | µg/kg dw | 5 | <5 | <5 |
| Phenazone | µg/kg dw | 5 | <5 | <5 |
| Primidone | µg/kg dw | 5 | <5 | <5 |
| Progesterone | µg/kg dw | 5 | <5 | <5 |
| Propranolol | µg/kg dw | 5 | <5 | <5 |
| Quetiapine | µg/kg dw | 5 | <5 | <5 |
| Ronidazole | µg/kg dw | 5 | <5 | <5 |
| Salbutamol | µg/kg dw | 5 | <5 | <5 |
| Sotalol | µg/kg dw | 5 | <5 | <5 |
| Sulfachloropyridazine | µg/kg dw | 5 | <5 | <5 |
| Sulfadiazine | µg/kg dw | 5 | <5 | <5 |
| Sulfadimethoxine | µg/kg dw | 5 | <5 | <5 |
| Sulfadimidine | µg/kg dw | 5 | <5 | <5 |
| Sulfamerazine | µg/kg dw | 5 | <5 | <5 |
| Sulfaquinoxaline | µg/kg dw | 10 | <10 | <10 |
| Tamoxifen | µg/kg dw | 10 | <10 | <10 |
| Terbutaline | µg/kg dw | 5 | <5 | <5 |
| Tiamulin | µg/kg dw | 5 | <5 | <5 |
| Triclocarban | µg/kg dw | 5 | <5 | <5 |
| Trimethoprim | µg/kg dw | 5 | <5 | <5 |
| Tylosin | µg/kg dw | 5 | <5 | <5 |
| Warfarin | µg/kg dw | 5 | <5 | <5 |
| 4-dimethylaminoantipyrine | µg/kg dw | 25 | <25 | <25 |

# Appendix 5 – PHREEQC input data

## Solution speciation (C3)

```
SOLUTION 1 C3_inflow
    temp      15.7
    pH        6.08
    pe         0 #Eh was not
measured
    redox     pe
    units     mg/l
    density   1
    Al        0.014
    B         0.23
    Ba        0.0673
    C           388 as HCO3
#average   values   of   HCO3
measured at Column 8 inflow
    Ca        29.4
    Cu        0.006
    Fe        0.03
    K         16.7
    Mg        17.4
    Mn        0.07
    N(-3)     32.8
    N(3)      0.02
    N(5)      0.3
    Na        58
    P         4.73
    S(6)      88
    Zn        0.03
    -water    1 # kg
SOLUTION                    2
C3_outflow_average_concentr
ation
    temp      20
    pH        7.37
    pe         0 #Eh was not
measured
    redox     pe
    units     mg/l
    density   1
    Al        0.02
    B         0.3
    Ba        0.2
    C           440 as HCO3
#average   values   of   HCO3
measured at Column 8 outflow
    Ca        76
    Cu        0.01
    Fe        0.02
    K         10
    Mg        30
    Mn        0.05
    N(-3)     1
    N(3)      1.2
    N(5)      0.86
    Na        39
    P         0.5
    S(6)      8.9
    Zn        0.003
    -water    1 # kg
SOLUTION 3 C3_outflow_80min
    temp      20.1
    pH        7.45
    pe        0
    redox     pe
    units     mg/l
    density   1
    B         0.56
    Cu        0.0113
    Zn        0
    N(-3)     0.193
    N(5)      3.33
    N(3)      1.45
    S(6)      0
    Al        0.202
    Ba        0.1
    Ca        33
    Fe        0.154
    Li        0.0011
    Mg        10.8
    Mn        0.00844
    P         0.132
    K         3.19
    Na        3.5
    C         440 as HCO3
    -water    1 # kg
SOLUTION 4 C3_outflow_169min
    temp      19.38
    pH        6.88
    pe        0
    redox     pe
    units     mg/l
    density   1
    B         0.285
    Cu        0.0128
    Zn        0.0039
    N(-3)     0.48
    N(5)      3.13
    N(3)      7.53
    S(6)      0
    Al        0.013
    Ba        0.202
    Ca        76.2
    Fe        0.0124
    Li        0
    Mg        28.8
    Mn        0.00488
    P         0.209
    K         10.9
    Na        12
    C         440 as HCO3
    -water    1 # kg
SOLUTION 5 C3_outflow_297min
    temp      20.8
    pH        7.35
    pe        0
    redox     pe
    units     mg/l
    density   1
    B         0.219
    Cu        0.012
    Zn        0.0037
    N(-3)     0.611
    N(5)      0.86
    N(3)      2.74
    S(6)      0
    Al        0
    Ba        0.261
    Ca        95.6
    Fe        0.0093
    Li        0
    Mg        37.3
    Mn        0.00548
    P         0.237
    K         7.58
    Na        17.4
    C         440 as HCO3
    -water    1 # kg
SOLUTION 6 C3_outflow_413min
    temp      20.6
    pH        7.2
    pe        0
    redox     pe
    units     mg/l
    density   1
    Al        0
    B         0.184
    Ba        0.275
    C         440 as HCO3
    Ca        99.7
    Cu        0.0112
    Fe        0.0084
    K         34.3
    Li        0
    Mg        39.7
    Mn        0.00917
    N(-3)     0.404
    N(3)      0.323
    N(5)      0
    Na        18.4
    P         0.265
    S(6)      0
    Zn        0.006
    -water    1 # kg
SOLUTION                    7
C3_outflow_1352min
    temp      20
    pH        7.2
    pe        0
    redox     pe
    units     mg/l
    density   1
    B         0.281
    Cu        0.0068
    Zn        0
    N(-3)     0.767
    N(5)      0
    N(3)      0.0132
    S(6)      0
    Al        0
    Ba        0.294
    Ca        87.4
    Fe        0.0127
    Li        0
    Mg        36.8
    Mn        0.0316
    P         0.431
    K         5.67
    Na        33.6
    C         440 as HCO3
    -water    1 # kg
SOLUTION                    8
C3_outflow_1673min
    temp      20
    pH        7.2
    pe        0
    redox     pe
    units     mg/l
    density   1
    B         0.296
    Cu        0.0056
    Zn        0.0038
    N(-3)     0.777
    N(5)      0
    N(3)      0.0126
    S(6)      0
    Al        0
    Ba        0.284
    Ca        79.1
    Fe        0.0115
    Li        0
    Mg        33.4
    Mn        0.0337
    P         0.5
    K         17.5
    Na        49.9
    C         440 as HCO3
    -water    1 # kg
SOLUTION                    9
C3_outflow_1949min
    temp      19.6
    pH        6.95
    pe        0
    redox     pe
    units     mg/l
    density   1
    Al        0.014
    B         0.258
    Ba        0.258
    C         440 as HCO3
    Ca        74.6
    Cu        0.0049
    Fe        0.0135
    K         10.8
    Li        0
    Mg        30.6
    Mn        0.034
    N(-3)     0.826
    N(3)      0.009
    N(5)      0
    Na        50.3
    P         0.548
    S(6)      6.9
    Zn        0.0046
    -water    1 # kg
SOLUTION                   10
C3_outflow_2773min
    temp      19.6
```

```
    pH          6.96
    pe          0
    redox       pe
    units       mg/l
    density     1
    B           0.258
    Cu          0.0046
    Zn          0
    N(-3)       1.13
    N(5)        0
    N(3)        0.0137
    S(6)        10.9
    Al          0.012
    Ba          0.228
    Ca          76.1
    Fe          0.0136
    Li          0
    Mg          32.2
    Mn          0.0471
    P           0.547
    K           6
    Na          57.1
    C           440 as HCO3
    -water      1 # kg
SOLUTION                    11
C3_outflow_3254min
    temp        19.1
    pH          9.48
    pe          0
    redox       pe
    units       mg/l
    density     1
    B           0.217
    Cu          0.0043
    Zn          0
    N(-3)       2
    N(5)        0
    N(3)        0.0144
    S(6)        18.4
    Al          0.014
    Ba          0.256
    Ca          72.6
    Fe          0.0113
    Li          0
    Mg          29.4
    Mn          0.129
    P           0.576
    K           6.69
    Na          59.3
    C           440 as HCO3
    -water      1 # kg
SOLUTION                    12
C3_outflow_4691min
    temp        18.9
    pH          7.22
    pe          0
    redox       pe
    units       mg/l
    density     1
    B           0.256
    Cu          0.0043
    Zn          0
    N(-3)       3.17
    N(5)        0
    N(3)        0.0174
    S(6)        27.1
    Al          0.01
    Ba          0.253
    Ca          72.5
    Fe          0.0098
    Li          0
    Mg          30.8
    Mn          0.145
    P           0.628
    K           6.74
    Na          61.3
    C           440 as HCO3
    -water      1 # kg
SOLUTION                    13
C3_outflow_6131min
    temp        18.7
    pH          7.08
    pe          0
    redox       pe
    units       mg/l
    density     1
    B           0.268
    Cu          0.0046
    Zn          0
    N(-3)       4.64
    N(5)        0
    N(3)        0.0201
    S(6)        5
    Al          0.011
    Ba          0.263
    Ca          74.9
    Fe          0.0083
    Li          0
    Mg          31.7
    Mn          0.187
    P           0.517
    K           7.53
    Na          66.4
    C           440 as HCO3
    -water      1 # kg
```

## Solution speciation (C4)

```
SOLUTION 1 C4_inflow
    temp        11.7
    pH          7.6
    pe          2.95
    redox       pe
    units       mg/l
    density     1
    B           0.235
    Cu          0
    Zn          0.0027
    N(-3)       34.2
    N(5)        0
    N(3)        0
    S(6)        64.7
    Al          0.011
    Ba          0.0523
    Ca          43.6
    Fe          0.0408
    Li          0.0012
    Mg          29
    Mn          0.0387
    P           2.79
    K           14.8
    Na          71.6
    Cl          91.1
    C             338 as HCO3
#average  values  of  HCO3
measured at Column 8 inflow
    -water      1 # kg
SOLUTION                    2
C4_outflow_average_concentr
ations
    temp        16.575
    pH          8.18
    pe          -0.08123
    redox       pe
    units       mg/l
    density     1
    B           0.758
    Cu          0.01
    Zn          0.006
    N(-3)       0.647
    N(5)        12.53
    N(3)        3.5068
    S(6)        60.5
    Al          0.015
    Ba          0.442
    Ca          103
    Fe          0.00664
    Li          0
    Mg          45.8
    Mn          0.055
    P           0.1023
    K           15.84
    Na          22.53
    Cl          97.99
    C             440 as HCO3
#average  values  of  HCO3
measured at Column 8 outflow
    -water      1 # kg
SOLUTION 3 C4_outflow_241min
    temp        16.2
    pH          6.98
    pe          0.18
    redox       pe
    units       mg/l
    density     1
    B           0.661
    Cu          0.0102
    Zn          0.0044
    N(-3)       0.255
    N(5)        9.89
    N(3)        1.48
    S(6)        0
    Al          0.018
    Ba          0.256
    Ca          33.7
    Fe          0.008
    Li          0
    Mg          12.4
    Mn          0.00216
    P           0.157
    K           60.5
    Na          4.34
    Cl          70.8
    C           440 as HCO3
    -water      1 # kg
SOLUTION 4 C4_outflow_381min
    temp        15.9
    pH          6.46
    pe          0.614
    redox       pe
    units       mg/l
    density     1
    B           0.779
    Cu          0.0123
    Zn          0.0088
    N(-3)       0.662
    N(5)        19.3
    N(3)        4.36
    S(6)        49.8
    Al          0.01
    Ba          0.456
    Ca          110
    Fe          0.007
    Li          0
    Mg          47.6
    Mn          0.0188
    P           0.092
    K           16.5
    Na          18.4
    Cl          103
    C           440 as HCO3
    -water      1 # kg
SOLUTION                    5
C4_outflow_1336min
    temp        16.2
    pH          6.98
    pe          0.18
    redox       pe
    units       mg/l
    density     1
    B           0.775
    Cu          0.0143
    Zn          0.0068
    N(-3)       0.653
    N(5)        8.4
    N(3)        18.6
    S(6)        51.7
    Al          0.015
    Ba          0.452
    Ca          113
    Fe          0.0084
    Li          0
    Mg          48.6
    Mn          0.0251
    P           0.103
    K           6.61
    Na          18.4
    Cl          95.1
    C           440 as HCO3
    -water      1 # kg
SOLUTION                    6
C4_outflow_1511min
    temp        16.5
    pH          7.51
    pe          -0.255
```

```
    redox     pe
    units     mg/l
    density   1
    B         0.763
    Cu        0.0129
    Zn        0.0064
    N(-3)     0.691
    N(5)      0
    N(3)      0.0413
    S(6)      64
    Al        0.014
    Ba        0.491
    Ca        118
    Fe        0.0067
    Li        0
    Mg        52.5
    Mn        0.026
    P         0.084
    K         6.4
    Na        22.4
    Cl        104
    C         440 as HCO3
    -water    1 # kg
SOLUTION                  7
C4_outflow_1596min
    temp      16.2
    pH        6.98
    pe        0.18
    redox     pe
    units     mg/l
    density   1
    B         0.761
    Cu        0.0116
    Zn        0.0094
    N(-3)     0.692
    N(5)      0
```

```
    N(3)      0.0216
    S(6)      64.4
    Al        0.013
    Ba        0.47
    Ca        116
    Fe        0.0066
    Li        0
    Mg        51.7
    Mn        0.0172
    P         0.09
    K         7.81
    Na        23.7
    Cl        106
    C         440 as HCO3
    -water    1 # kg
SOLUTION                  8
C4_outflow_1854min
    temp      16.2
    pH        6.98
    pe        0.18
    redox     pe
    units     mg/l
    density   1
    B         0.811
    Cu        0.0083
    Zn        0.0042
    N(-3)     0.499
    N(5)      0
    N(3)      0.0286
    S(6)      64.5
    Al        0.017
    Ba        0.491
    Ca        118
    Fe        0.0054
    Li        0
    Mg        54
```

```
    Mn        0.0819
    P         0.104
    K         6.67
    Na        30.7
    Cl        106
    C         440 as HCO3
    -water    1 # kg
SOLUTION                  9
C4_outflow_3084min
    temp      16.2
    pH        6.98
    pe        0.18
    redox     pe
    units     mg/l
    density   1
    B         0.755
    Cu        0.0062
    Zn        0
    N(-3)     1.08
    N(5)      0
    N(3)      0.0159
    S(6)      69
    Al        0.017
    Ba        0.478
    Ca        115
    Fe        0.0044
    Li        0
    Mg        53.8
    Mn        0.212
    P         0.086
    K         6.39
    Na        39.8
    Cl        101
    C         440 as HCO3
    -water    1 # kg
```

## Solution speciation (C8)

```
SOLUTION 1 C8_inflow
    temp      19
    pH        7.28
    pe        1.55
    redox     pe
    units     mg/l
    density   1
    Al        0.06
    B         0.72
    Ba        0.18
    C         338 as HCO3
    Ca        37.8
    Cl        118
    Cu        0.003
    Fe        0.06
    K         23.6
    Mg        28.4
    Mn        0.06
    N(-3)     48.9
    N(3)      0.01
    N(5)      2
    Na        92.5
    P         5.52
    S(6)      70.5
    -water    1 # kg
SOLUTION    2     C8_outflow
(average              outflow
concentrations)
    temp      20
    pH        7.36
    pe        -0.39
    redox     pe
    units     mg/l
    density   1
    Al        0.02
    B         0.4
    Ba        0.3
    C         440 as HCO3
    Ca        132
    Cl        117
    Cu        0.002
    Fe        0.05
    K         30
    Mg        40
    Mn        0.5
    N(-3)     2
    N(3)      4
```

```
    N(5)      140
    Na        83
    P         4
    S(6)      77
    -water    1 # kg

SOLUTION 3 C8_outflow_20min
    temp      21.7
    pH        7.07
    pe        0.25
    redox     pe
    units     mg/l
    density   1
    Al        0
    B         0.688
    Ba        0.425
    C         440 as HCO3
    Ca        125
    Cl        3.77
    Cu        0
    Fe        0.0138
    K         15
    Li        0
    Mg        36.3
    Mn        0.114
    N(-3)     0.699
    N(3)      0.132
    N(5)      10.2
    Na        7.18
    P         0.8
    S(6)      19.6
    Zn        0.0091
    -water    1 # kg
SOLUTION 4 C8_outflow_45min
    temp      20.9
    pH        6.27
    pe        1.06
    redox     pe
    units     mg/l
    density   1
    Al        0
    B         0.668
    Ba        0.78
    C         440 as HCO3
    Ca        244
    Cl        34.5
    Cu        0.003
```

```
    Fe        0.0141
    K         32.9
    Li        0
    Mg        75
    Mn        0.396
    N(-3)     1.23
    N(3)      0.331
    N(5)      399
    Na        20.8
    P         1.33
    S(6)      62.2
    Zn        0.012
    -water    1 # kg
SOLUTION 5 C8_outflow_75min
    temp      20.6
    pH        6.9
    pe        0.42
    redox     pe
    units     mg/l
    density   1
    B         0.7
    Cu        0.0106
    Zn        0.0103
    N(-3)     1.52
    N(5)      724
    N(3)      0.245
    S(6)      94.9
    Al        0.014
    Ba        0.842
    Ca        273
    Fe        0.0254
    Li        0.0487
    Mg        84.2
    Mn        0.426
    P         1.52
    K         36.9
    Na        49.5
    Cl        70.5
    C         440 as HCO3
    -water    1 # kg
SOLUTION 6 C8_outflow_120min
    temp      20.8
    pH        7.21
    pe        0.068
    redox     pe
    units     mg/l
    density   1
```

```
    Al          0
    B           0.841
    Ba          0.626
    C           440 as HCO3
    Cu          0.0013
    Fe          0.0114
    K           33
    Li          0.0119
    Mg          54.4
    Mn          0.273
    N(3)        0.359
    N(-3)       1.18
    N(5)        349
    Na          35.2
    P           1.66
    S(6)        63.3
    Zn          0
    Ca          171
    Cl          51.8
    -water      1 # kg
SOLUTION                    7
C8_outflow_1510min
    temp        23.1
    pH          7.61
    pe          -0.32
    redox       pe
    units       mg/l
    density     1
    Al          0
    B           0.734
    Ba          0.439
    C           440 as HCO3
    Cu          0.003
    Fe          0.012
    K           25.7
    Li          0.017
    Mg          31.5
    Mn          0.00107
    N(3)        0.199
    N(-3)       1.42
    N(5)        12.6
    Na          30.9
    P           1.34
    S(6)        34
    Zn          0
    Ca          102
    Cl          37
    -water      1 # kg
SOLUTION                    8
C8_outflow_1570min
    temp        23.4
    pH          7.3
    pe          -0.034
    redox       pe
    units       mg/l
    density     1
    Al          0
    B           0.691
    Ba          0.398
    C           440 as HCO3
    Ca          81.3
    Cl          34.7
    Cu          0.0033
    Fe          0.0147
    K           23.2
    Li          0.015
    Mg          24.2
    Mn          0.105
    N(-3)       1.33
    N(3)        0.159
    N(5)        12.3
    Na          26.8
    P           1.73
    S(6)        29.3
    Zn          0
    -water      1 # kg
SOLUTION                    9
C8_outflow_1630min
    temp        23.7
    pH          7.8
    pe          -0.51
    redox       pe
    units       mg/l
    density     1
    B           0.74
    Cu          0.0033
    Zn          0
    N(-3)       1.26
    N(5)        4.26
    N(3)        0.15
    S(6)        24.3
    Al          0.011
    Ba          0.356
    Ca          68.5
    Fe          0.0126
    Li          0.0136
    Mg          20.5
    Mn          0.0401
    P           1.84
    K           21.2
    Na          24.3
    Cl          34.3
    C           440 as HCO3
    -water      1 # kg
SOLUTION                   10
C8_outflow_2963min
    temp        23.9
    pH          7.8
    pe          -0.58
    redox       pe
    units       mg/l
    density     1
    B           0.757
    Cu          0.0025
    Zn          0
    N(-3)       1.5
    N(5)        0
    N(3)        0.12
    S(6)        21.1
    Al          0
    Ba          0.377
    Ca          80.5
    Fe          0.0097
    Li          0.0133
    Mg          23.5
    Mn          0.00107
    P           1.43
    K           23
    Na          25.7
    Cl          32.8
    C           440 as HCO3
    -water      1 # kg
SOLUTION                   11
C8_outflow_3053min
    temp        23.9
    pH          7.8
    pe          -0.58
    redox       pe
    units       mg/l
    density     1
    B           0.712
    Cu          0.0024
    Zn          0.0023
    N(-3)       1.29
    N(5)        8.25
    N(3)        0.529
    S(6)        22.2
    Al          0
    Ba          0.353
    Ca          73.2
    Fe          0.0115
    Li          0.0127
    Mg          21.2
    Mn          0.00263
    P           1.67
    K           23
    Na          25.8
    Cl          33.3
    C           440 as HCO3
    -water      1 # kg
SOLUTION                   12
C8_outflow_3113min
    temp        23.9
    pH          7.8
    pe          -0.58
    redox       pe
    units       mg/l
    density     1
    B           0.393
    Cu          0.0023
    Zn          0
    N(-3)       1.05
    N(5)        15.5
    N(3)        0.334
    S(6)        22
    Al          0
    Ba          0.203
    Ca          61.1
    Fe          0.0083
    Li          0.0107
    Mg          17.9
    Mn          0.00283
    P           1.78
    K           20
    Na          21.5
    Cl          34.2
    C           440 as HCO3
    -water      1 # kg
SOLUTION                   13
C8_outflow_7700min
    temp        24.8
    pH          7.15
    pe          -0.234
    redox       pe
    units       mg/l
    density     1
    B           0.728
    Cu          0.0025
    Zn          0.0093
    N(-3)       1.88
    N(5)        18.4
    N(3)        0.452
    S(6)        22.3
    Al          0
    Ba          0.398
    Ca          87.7
    Fe          0.0096
    Li          0.0123
    Mg          25.3
    Mn          0.264
    P           0.833
    K           24.5
    Na          28.7
    Cl          35.4
    C           440 as HCO3
    -water      1 # kg
SOLUTION                   14
C8_outflow_7830min
    temp        24.9
    pH          7.12
    pe          -0.23
    redox       pe
    units       mg/l
    density     1
    Al          0
    B           0.738
    Ba          0.6
    C           440 as HCO3
    Ca          162
    Cl          117
    Cu          0.0017
    Fe          0.0103
    K           34.2
    Li          0.0166
    Mg          46.9
    Mn          0.697
    N(-3)       2.66
    N(3)        3.88
    N(5)        222
    Na          40.9
    P           0.816
    S(6)        64.9
    Zn          0.0044
    -water      1 # kg
SOLUTION                   15
C8_outflow_20356min
    temp        24.3
    pH          6.83
    pe          0.12
    redox       pe
    units       mg/L
    density     1
    B           0.211
    Cu          0.0018
    Zn          0.0038
    N(-3)       4.31
    N(5)        479
    N(3)        2.92
    S(6)        282
    Al          0
    Ba          0.722
    Ca          290
    Fe          0.121
    Li          0.0245
```

```
    Mg          89.8
    Mn          1.94
    P           0.121
    K           50.5
    Na          250
    Cl          414
    C           455 as HCO3
    -water      1 # kg
SOLUTION                    16
C8_outflow_20776min
    temp        24.3
    pH          6.83
    pe          0.12
    redox       pe
    units       mg/l
    density     1
    B           0.615
    Cu          0.0036
    Zn          0.007
    N(-3)       1.74
    N(5)        648
    N(3)        10.2
    S(6)        225
    Al          0.233
    Ba          0.0354
    Ca          270
    Fe          0.288
    Li          0.0259
    Mg          82.5
    Mn          1.77
    P           0.369
    K           49.1
    Na          291
    Cl          353
    C           486 as HCO3
    -water      1 # kg
SOLUTION                    17
C8_outflow_22196min
    temp        18.4
    pH          7.35
    pe          -0.208
    redox       pe
    units       mg/l
    density     1
    B           0.165
    Cu          0.002
    Zn          0
    N(-3)       1.18
    N(5)        105
    N(3)        17.6
    S(6)        206
    Al          0
    Ba          0.484
    Ca          191
    Fe          0.0255
    Li          0.0243
    Mg          60.4
    Mn          1.01
    P           0.64
    K           42
    Na          267
    Cl          318
    C           715 as HCO3
    -water      1 # kg
SOLUTION                    18
C8_outflow_23026min
    temp        25
    pH          7.37
    pe          -0.191
    redox       pe
    units       mg/l
    density     1
    B           0.187
    Cu          0.0021
    Zn          0
    N(-3)       3.2
    N(5)        0
    N(3)        0.0121
    S(6)        207
    Al          0
    Ba          0.47
    Ca          184
    Fe          0.0255
    Li          0.0257
    Mg          55.8
    Mn          0.938
    P           0.92
    K           41.7
    Na          253
    Cl          314
    C           816 as HCO3
    -water      1 # kg
SOLUTION                    19
C8_outflow_30286min
    temp        12
    pH          7.29
    pe          -0.58
    redox       pe
    units       mg/l
    density     1
    B           0.156
    Cu          0.0023
    Zn          0
    N(-3)       9.75
    N(5)        439
    N(3)        3.84
    S(6)        126
    Al          0
    Ba          0.349
    Ca          139
    Fe          0.0962
    Li          0.0196
    Mg          47.2
    Mn          0.903
    P           0.461
    K           37
    Na          206
    Cl          197
    C           432 as HCO3
    -water      1 # kg
SOLUTION                    20
C8_outflow_33166min
    temp        15
    pH          8.24
    pe          -0.269
    redox       pe
    units       mg/l
    density     1
    B           0.174
    Cu          0.0021
    Zn          0
    N(-3)       5.67
    N(5)        109
    N(3)        2
    S(6)        72
    Al          0
    Ba          0.195
    Ca          74
    Fe          0.0201
    Li          0.0127
    Mg          23.3
    Mn          0.486
    P           0.818
    K           26.3
    Na          113
    Cl          102
    C           394 as HCO3
    -water      1 # kg
SOLUTION                    21
C8_outflow_40366min
    temp        4.6
    pH          7.3
    pe          -0.189
    redox       pe
    units       mg/l
    density     1
    B           0.206
    Cu          0.0016
    Zn          0
    N(-3)       3.3
    N(5)        151
    N(3)        2.57
    S(6)        49.4
    Al          0
    Ba          0.206
    Ca          82.8
    Fe          0.0574
    Li          0.0114
    Mg          25.7
    Mn          0.58
    P           1.02
    K           26
    Na          85.2
    Cl          83.1
    C           352 as HCO3
    -water      1 # kg
SOLUTION                    22
C8_outflow_44626min
    temp        5.7
    pH          7.15
    pe          -0.065
    redox       pe
    units       mg/l
    density     1
    Al          0
    B           0.164
    Ba          0.15
    C           319 as HCO3
    Ca          59.8
    Cl          48.9
    Cu          0.0013
    Fe          0.036
    K           21.5
    Li          0.0091
    Mg          18.2
    Mn          0.389
    N(-3)       1.6
    N(3)        1.93
    N(5)        45.3
    Na          52.3
    P           1.42
    S(6)        30.4
    Zn          0
    -water      1 # kg
SOLUTION                    23
C8_outflow_53313min
    temp        6.9
    pH          6.9
    pe          -0.475
    redox       pe
    units       mg/l
    density     1
    Al          0
    B           0.22
    Ba          0.176
    C           353 as HCO3
    Ca          79.2
    Cl          69.3
    Cu          0.0014
    Fe          0.0573
    K           24.2
    Li          0.0089
    Mg          23.8
    Mn          0.486
    N(-3)       0.659
    N(3)        1.66
    N(5)        49.8
    Na          45.6
    P           1.09
    S(6)        38.3
    Zn          0
    -water      1 # kg
SOLUTION                    24
C8_outflow_60496min
    temp        9.1
    pH          8.01
    pe          -1.008
    redox       pe
    units       mg/l
    density     1
    Al          0
    B           0.188
    Ba          0.148
    C           345 as HCO3
    Ca          70
    Cl          62.6
    Cu          0.0011
    Fe          0.0561
    K           21.9
    Li          0.0086
    Mg          21
    Mn          0.42
    N(-3)       1.02
    N(3)        0.848
    N(5)        0
    Na          44.2
    P           1.43
    S(6)        36.6
    Zn          0
    -water      1 # kg
SOLUTION                    25
C8_outflow_62326min
    temp        13.1
    pH          7.55
```

```
    pe          -0.484
    redox       pe
    units       mg/l
    density     1
    B           0.239
    Cu          0.0011
    Zn          0
    N(-3)       0.853
    N(5)        0
    N(3)        0.184
    S(6)        16.3
    Al          0
    Ba          0.189
    Ca          78.9
    Fe          0.112
    Li          0.0106
    Mg          26.4
    Mn          0.52
    P           1.58
    K           25.7
    Na          46.6
    Cl          45
    C           410 as HCO3
    -water      1 # kg
SOLUTION                    26
C8_outflow_64846min
    temp        20.8
    pH          7.72
    pe          -0.635
    redox       pe
    units       mg/l
    density     1
    Al          0
    B           0.257
    Ba          0.214
    C           379 as HCO3
    Ca          95.2
```

```
    Cl          89.4
    Cu          0
    Fe          0.133
    K           26.6
    Li          0.011
    Mg          31.1
    Mn          0.676
    N(-3)       1.11
    N(3)        0.181
    N(5)        0
    Na          47.7
    P           1.55
    S(6)        46.1
    Zn          0
    -water      1 # kg
SOLUTION                    27
C8_outflow_65326min
    temp        12.3
    pH          7.74
    pe          -0.703
    redox       pe
    units       mg/l
    density     1
    Al          0
    B           0.308
    Ba          0.24
    C           347 as HCO3
    Ca          95.5
    Cl          110
    Cu          0.0011
    Fe          0.148
    K           26.4
    Li          0.0112
    Mg          30.7
    Mn          0.659
    N(-3)       2.14
    N(3)        0.079
```

```
    N(5)        0
    Na          56.7
    P           1.6
    S(6)        56.4
    Zn          0
    -water      1 # kg
SOLUTION                    28
C8_outflow_66286min
    temp        24.3
    pH          7.01
    pe          0.189
    redox       pe
    units       mg/l
    density     1
    B           0.117
    Cu          0
    Zn          0
    N(-3)       0.523
    N(5)        0
    N(3)        0.0292
    S(6)        51.2
    Al          0
    Ba          0.18
    Ca          97.6
    Fe          0.136
    Li          0.0114
    Mg          30.9
    Mn          0.645
    P           1.52
    K           26.8
    Na          70.9
    Cl          117
    C           367 as HCO3
    -water      1 # kg
```

## Inverse modeling (C3)

```
SOLUTION 1 C3_inflow
    temp        15.7
    pH          6.08
    pe           0 #Eh was not
measured
    redox       pe
    units       mg/l
    density     1
    C             388 as HCO3
#average   values   of   HCO3
measured at Column 8 inflow
    Ca          29.4
    Mg          17.4
    Na          58
    -water      1 # kg

SOLUTION 3 C3_outflow_80min
    temp        20.1
    pH          7.45
    pe          0
    redox       pe
    units       mg/l
    density     1
    Ca          33
    Mg          10.8
    Na          3.5
    C           440 as HCO3
    -water      1 # kg

SOLUTION 4 C3_outflow_169min
    temp        19.38
    pH          6.88
    pe          0
    redox       pe
    units       mg/L
    density     1
    Ca          76.2
    Mg          28.8
    Na          12
    C           440 as HCO3
    -water      1 # kg
SOLUTION 5 C3_outflow_297min
    temp        20.8
    pH          7.35
    pe          0
    redox       pe
    units       mg/l
    density     1
```

```
    Ca          95.6
    Mg          37.3
    Na          17.4
    C           440 as HCO3
    -water      1 # kg
SOLUTION 6 C3_outflow_413min
    temp        20.6
    pH          7.2
    pe          0
    redox       pe
    units       mg/l
    density     1
    C           440 as HCO3
    Ca          99.7
    Mg          39.7
    Na          18.4
    -water      1 # kg
SOLUTION                    7
C3_outflow_1352min
    temp        20
    pH          7.2
    pe          0
    redox       pe
    units       mg/l
    density     1
    Ca          87.4
    Mg          36.8
    Na          33.6
    C           440 as HCO3
    -water      1 # kg
SOLUTION                    8
C3_outflow_1673min
    temp        20
    pH          7.2
    pe          0
    redox       pe
    units       mg/l
    density     1
    Ca          79.1
    Mg          33.4
    Na          49.9
    C           440 as HCO3
    -water      1 # kg
SOLUTION                    9
C3_outflow_1949min
    temp        19.6
    pH          6.95
    pe          0
```

```
    redox       pe
    units       mg/l
    density     1
    C           440 as HCO3
    Ca          74.6
    Mg          30.6
    Na          50.3
    -water      1 # kg
SOLUTION                    10
C3_outflow_2773min
    temp        19.6
    pH          6.96
    pe          0
    redox       pe
    units       mg/l
    density     1
    Ca          76.1
    Mg          32.2
    Na          57.1
    C           440 as HCO3
    -water      1 # kg
SOLUTION                    11
C3_outflow_3254min
    temp        19.1
    pH          9.48
    pe          0
    redox       pe
    units       mg/l
    density     1
    Ca          72.6
    Mg          29.4
    Na          59.3
    C           440 as HCO3
    -water      1 # kg
SOLUTION                    12
C3_outflow_4691min
    temp        18.9
    pH          7.22
    pe          0
    redox       pe
    units       mg/l
    density     1
    Ca          72.5
    Mg          30.8
    Na          61.3
    C           440 as HCO3
    -water      1 # kg
```

```
SOLUTION                  13
C3_outflow_6131min
    temp      18.7
    pH        7.08
    pe        0
    redox     pe
    units     mg/l
    density   1
    Ca        74.9
    Mg        31.7
    Na        66.4
    C         440 as HCO3
    -water    1 # kg
INVERSE_MODELING 1
    -solutions     1       3
    -uncertainty         0.5
0.5
    -phases
        Calcite
        Dolomite
        Halite
        CaX2
        NaX
        MgX2
    -balances
        Cl               0.5
0.5
    -tolerance         1e-10
    -mineral_water     true

INVERSE_MODELING 2
    -solutions     1       4
    -uncertainty         0.5
0.5
    -phases
        Calcite
        Dolomite
        Halite
        CaX2
        NaX
        MgX2
    -balances
        Cl               0.5
0.5
    -tolerance         1e-10
    -mineral_water     true
INVERSE_MODELING 3
    -solutions     1       5
    -uncertainty         0.5
0.5
    -phases
        Calcite
        Dolomite
        Halite
        CaX2
        NaX
        MgX2
    -balances
        Cl               0.5
0.5
    -tolerance         1e-10
    -mineral_water     true
INVERSE_MODELING 4
    -solutions     1       6
    -uncertainty         0.5
0.5
    -phases
        Calcite
        Dolomite
        Halite
        CaX2
        NaX
        MgX2
    -balances
        Cl               0.5
0.5
    -tolerance         1e-10
    -mineral_water     true
INVERSE_MODELING 5
    -solutions     1       7
    -uncertainty         0.5
0.5
    -phases
        Calcite
        Dolomite
        Halite
        CaX2
        NaX
```

```
        MgX2
    -balances
        Cl               0.5
0.5
    -tolerance         1e-10
    -mineral_water     true
INVERSE_MODELING 6
    -solutions     1       8
    -uncertainty         0.5
0.5
    -phases
        Calcite
        Dolomite
        Halite
        CaX2
        NaX
        MgX2
    -balances
        Cl               0.5
0.5
    -tolerance         1e-10
    -mineral_water     true
INVERSE_MODELING 7
    -solutions     1       9
    -uncertainty         0.5
0.5
    -phases
        Calcite
        Dolomite
        Halite
        CaX2
        NaX
        MgX2
    -balances
        Cl               0.5
0.5
    -tolerance         1e-10
    -mineral_water     true
INVERSE_MODELING 8
    -solutions     1      10
    -uncertainty         0.5
0.5
    -phases
        Calcite
        Dolomite
        Halite
        CaX2
        NaX
        MgX2
    -balances
        Cl               0.5
0.5
    -tolerance         1e-10
    -mineral_water     true
INVERSE_MODELING 9
    -solutions     1      11
    -uncertainty         0.5
0.5
    -phases
        Calcite
        Dolomite
        Halite
        CaX2
        NaX
        MgX2
    -balances
        Cl               0.5
0.5
    -tolerance         1e-10
    -mineral_water     true
INVERSE_MODELING 10
    -solutions     1      12
    -uncertainty         0.5
0.5
    -phases
        Calcite
        Dolomite
        Halite
        CaX2
        NaX
        MgX2
    -balances
        Cl               0.5
0.5
    -tolerance         1e-10
    -mineral_water     true
INVERSE_MODELING 11
    -solutions     1      13
```

```
    -uncertainty         0.5
0.5
    -phases
        Calcite
        Dolomite
        Halite
        CaX2
        NaX
        MgX2
    -balances
        Cl               0.5
0.5
    -tolerance         1e-10
    -mineral_water     true
```